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REFERENCE

Lane, B. H., 1935, Suggestions to authors of papers submitted for publication by the United States Geological Survey: U. S. Geol. Survey, Washington, D. C. (For sale by Superintendent of Documents, Washington, D. C. 40c.)

ANNOUNCEMENT

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[American Journal of Science, Vol. 255, Summer 1957, P. 447-460]

American Journal of Science

SUMMER 1957

THE LATE-GLACIAL CHRONOLOGY OF EUROPE—A DISCUSSION

H. E. WRIGHT, JR.*

ABSTRACT. Recent refinements in pollen analysis plus the introduction of radiocarbon dating have increased understanding of the chronology of climatic fluctuations, morainic development, and vegetational succession in Europe during the Late-Glacial phase of the Weichsel or Würm glaciation. The Alleröd warm fluctuation in the pollen diagrams provides the key horizon for correlation over a broad area; it is firmly related to ice retreat prior to the formation of the Central Swedish-Salpausselkä moraines on the basis of varve chronology, radiocarbon dating, and the location of Alleröd-bearing bogs with respect to the Scandinavian moraines. The Alleröd interval is identifiable over a broad area from the glacial region southward to the Alps, and its correlation is supported by radiocarbon dating and by the occurrence of volcanic ash within it.

An earlier warm fluctuation (Bölling) is becoming widely recognized in pollen diagrams from Denmark and adjacent regions, and its correlation with a retreatal phase of the Scandinavian ice sheet is being studied. Correlation of the Bölling interstadial with the moramic sequence in the Alps is not yet firm, but radiocarbon dating has not yet been widely applied in the Alpine region.

The pollen diagrams of the periglacial zone are generally bottomed on a treeless tundra phase that fades downward into unfossiliferous sediments of the High-Glacial phases, when, according to Gross, frost action inhibited orderly accumulation of pollen-bearing sediments. Correlation of earlier stages between the Alps and the Scandinavian ice margin is thus not aided by pollen analysis nor as yet by radiocarbon dating. The latter technique can be applied to much of this time range, however, so firming of the correlations can soon be expected.

INTRODUCTION

The absolute chronology of the Late-Glacial phase of northern Europe, as worked out during the past 50 years on the basis of moraines, varved clays, drainage of the Baltic Sea, and pollen profiles, has not required the degree of modification necessitated in the correlative American chronology upon the introduction of the radiocarbon-dating method. The DeGeer (1940) chronology for the last 11,000 years has been confirmed by radiocarbon dates for the Alleröd interstadial (centering around 11,500 years ago), a subdivision of the Late-Glacial based on a zone in the pollen profiles. The new techniques of counting non-arboreal pollen and of determining tree-pollen frequency have permitted the subdivision of the very basal portions of the pollen profiles so that the inferred climatic fluctuations during the earlier stages of ice retreat may be correlated with ice borders, periglacial features, and the movements of Early Man and his mammalian associates.

The following discussion is precipitated by a comprehensive summary by Hugo Gross (1954, 1955)[1] of Bamberg, Germany, of the status of Late-Glacial chronology of Europe, with especial reference to the Alleröd interstadial and

* The writer is pleased to acknowledge the criticisms of a draft of this discussion proffered by C. S. Stearns, Sheldon Judson, and Meyer Rubin.

[1] The writer has prepared mimeographed translations of the two Gross papers for distribution to interested persons.

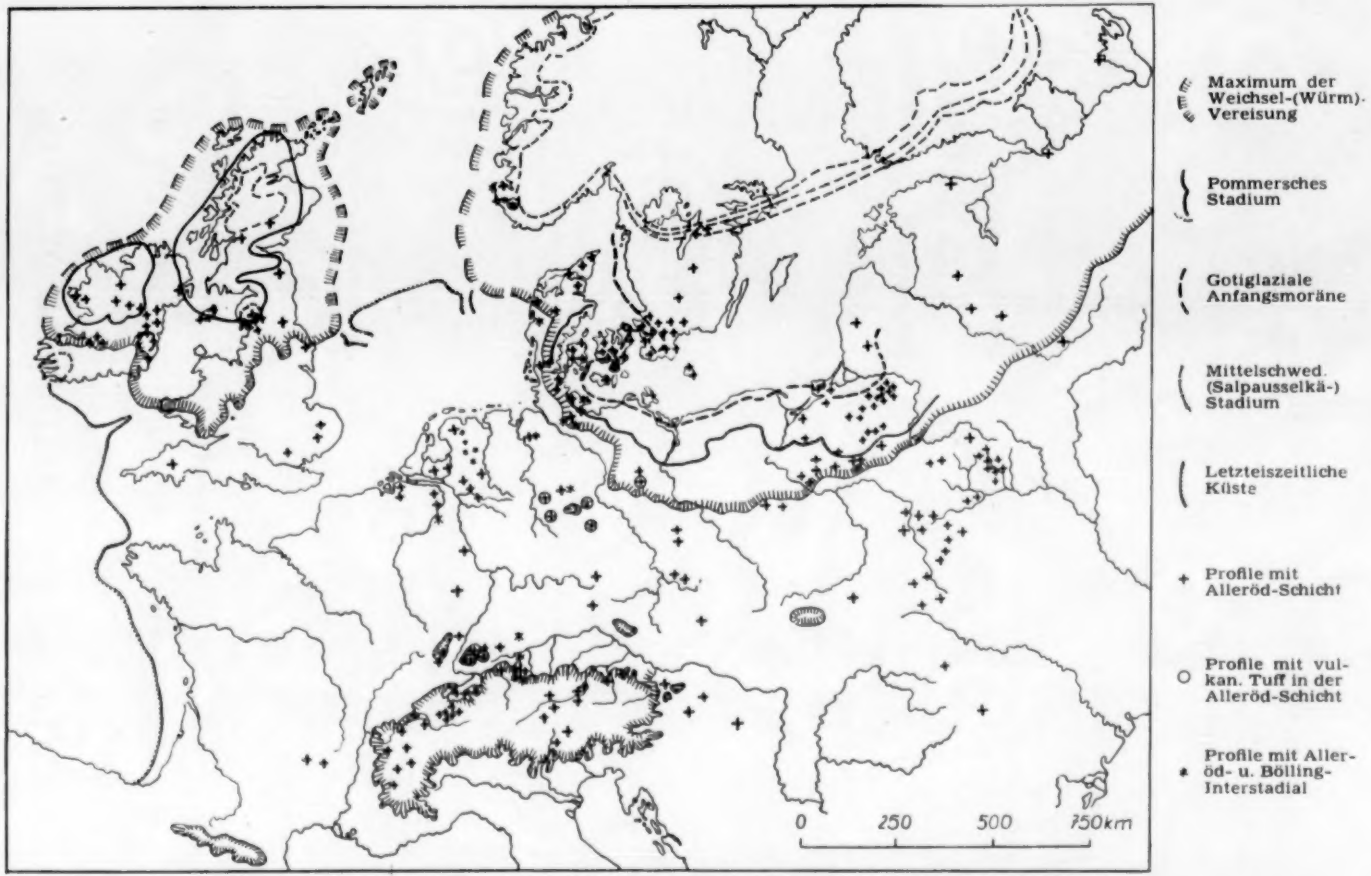

Fig. 1. Distribution of Late Glacial Interstadial occurrences in Europe (Gross, 1954).

to the new radiocarbon dates. Gross has been occupied for many years with the study of the geology, palynology, paleontology, and archeology of the Alleröd interstadial and other Late-Glacial phases, especially in East Prussia (Gross, 1937, 1951) and more recently was among the first Europeans to offer a comprehensive discussion of the effects of radiocarbon dating on problems in Pleistocene chronology (Gross, 1952). The discussion here is concerned with some of the central problems considered by Gross, and is amplified by reference to some of the many other recent papers that deal with this matter. American readers interested in the Pleistocene of Europe probably rely for most of their information on the summaries by Deevey (1949, 1953), and Zeuner (1952) and the occasional reviews and comments by Antevs (1953). The flood of research papers, monographs, and books which have appeared since the war from Europe, particularly Germany, is so impressive that any systematic survey is difficult on the part of one not familiar with the area and the problems. Three journals (*Eiszeitalter und Gegenwart, Zeitschrift für Gletscherkunde und Glazialgeologie*, and *Quaternaria*) are devoted almost solely to studies of glacial geology and Pleistocene history, and in addition pertinent papers appear frequently in the host of general and regional journals. A few authors, particularly Scandinavian, have published in English, and an increasing number of papers bear English abstracts. American Pleistocene geologists, however, cannot afford to ignore the rapid European progress on problems of mutual interest that are concerned ultimately with Pleistocene climate and have implications concerning world-wide climatic changes.

ALLEROD INTERSTADIAL

The Alleröd zone in the pollen profile is the key horizon for relating the pollen record to the glacial stratigraphy and morphology (table 1). In northern Europe the Alleröd is identified generally by a temporary decrease in the count of non-arboreal pollen (NAP), an increase in the absolute frequency of tree pollen, and among the tree pollen an increase in birch, pine, and other indicators of a cool-temperate climate. The zones above and below are commonly characterized by pollen of the tundra plant *Dryas octapetala*, and are called respectively the Older and Younger Tundra phases (or Older and Younger Dryas). Following the Younger Tundra zone comes the succession of Preboreal, Boreal, etc. phases of the Post-Glacial long established in the pollen stratigraphy of northern Europe.

Where the Alleröd layer occurs in lake sediments, it is commonly coincident with mud rich in organic matter compared to the mineral clays or sands of the Tundra zones below and above. The Alleröd layer has been identified in a wide variety of other environments, such as sands, alluvial soils, and even marine sediments.

Radiocarbon dating of the Alleröd pollen zone has been extremely successful (table 2). An early group of four dates from the Chicago laboratory for samples from the British Isles and from Wallensen, Germany, was followed by analyses at Copenhagen of 10 samples carefully collected from various laminae in the upper half of the Alleröd beds at an exposure at the Ruds Vedby brickwork, Denmark (Iversen, 1953; Krog, 1954). The Ruds Vedby

TABLE 1

Phases of the Last Glaciation in Europe (Gross, 1954)
Modified in last column by addition of new radiocarbon dates

Epoch	According to DeGeer	Positions of Ice Border: Weichsel	Positions of Ice Border: Würm	Period of Vegetational History: Phase	Period of Vegetational History: Plant Cover	Climate	Zone (Firbas)	C-14 Dates (BP)
Postglacial (beginning)	Finiglacial (beginning)			Pre-boreal	Pine-birch forest	Persisting warmth	IV	10,300
Late-Glacial	Gotiglacial	Salpausselkä II Central Swedish ice-border belt Salpausselkä I	Final Glaciation of the Alps (Daun, Gschnitz, Schlern)	Younger Dryas	Park tundra	Very cold maritime "subarctic"	III	10,750
		Central southern Sweden, Leningrad		Alleröd inter-stadial	Pine phase Sparse forest cover Birch phase	Moderate "subarctic" to temperate	IIb IIa	11,800
				Older Dryas	Park tundra Tundra	Continental "subarctic"	Ic	12,300
		Langeland N. Pomeranian		Bölling interst.	Park tundra	Slight warming	Ib	13,000
	Daniglacial	Samlund	Ammersee stadial (Bühl in broad sense)	Oldest Dryas	Treeless tundra	Cold continental: "Arctic" / "Subarctic"	Ia / Ia?	15,150
High-Glacial (end)	Pomeranian	S. Pomeranian end moraines	Inner young moraines (Zürich, Singen, Olkofen)		Frost rubble Tundra	"Arctic"		15,750

series has fine internal consistency and shows that the Alleröd started before 12,000 years ago and extended until about 10,800. The early Chicago date of 11,044 for the Alleröd at Wallensen northwest of the Harz Mountains in central Germany (Firbas, 1954a) has been confirmed by new determinations at Copenhagen (11,160) and Heidelberg (11,800). An additional Alleröd date comes from Bölling Lake in Denmark (11,700); the mean of unpublished analyses of Dutch Alleröd samples at the Groningen Laboratory is 10,980.

TABLE 2

Radiocarbon Dates from the Late-Glacial of Europe

Sample No.	Description	Age (years BP)
POLLEN-DATED SAMPLES		
Younger Tundra Phase		
K-111[1]	Bölling Lake, Denmark. Lake mud. Top of Younger Tundra.	10,300 ± 350
GRO-961[4]	Schalkenmehren crater, Eifel Mountains, central Germany. Lake mud over latest tuff.	10,550 ± 100
GRO-458[4]	Schalkenmehren crater. Material similar to GRO-961.	10,770 ± 250
K-110[1]	Bölling Lake, Denmark. Lake mud. Base of Younger Tundra. Mean of two measurements.	10,770 ± 300
Alleröd Phase		
	Ruds Vedby, Denmark[1,2,3]. Arranged in order from top of Alleröd down to middle. Lower part of exposure not sampled.	
K-101, 102, 103.	Wood, peaty lake mud, and calcareous lake mud respectively. Boundary Alleröd/Younger Tundra. Mean of 5 measurements.	10,750 ± 200
K-113	Lake marl. End of Alleröd maximum.	10,930 ± 380
K-104	Calcareous lake mud, just below K-113. Mean of two measurements.	10,990 ± 240
K-105	Calcareous lake mud. Middle of Alleröd.	11,800 ± 410
K-106	Lake marl, just below K-105	11,880 ± 340
	Wallensen im Hils, NW Germany[7]. Mud directly above Laacher volcanic tuff. Upper part of Alleröd.	
C-337[6]	Peaty mud.	11,044 ± 500
K-107[1]	Same as C-337.	11,160 ± 320
H- ?	Coarse detrital gyttja.	11,800 ± 300
Bölling Lake, Denmark.[1]		
K-102	Lake mud. Mean of 2 measurements.	11,700 ± 360
British Isles[6,8]		
C-341	Hawkes Tor, Cornwall, England. Peat. Alleröd[8] or Younger Tundra[2].	9861 ± 500
C-444	Neasham, northern England. Lake mud.	10,851 ± 630
C-355	Knocknacran, Ireland. Lake mud.	11,310 ± 720
Holland[5]		
GRO-?	Mean of several samples.	10,980
Older Tundra Phase[9]		
H 77/54	Gaterslebener Lake, near Aschersleben, central Germany. Wood from clay-mud. Beginning of Older Tundra.	12,300 ± 260
Bölling Phase[9]		
H 106/89	Gaterslebener Lake, near Aschersleben, central Germany. Sedge peat. Before or at beginning of Bölling.	12,700 ± 320
H 88/74	Material similar to H 106/89.	13,250 ± 280

TABLE 2 (continued)

Sample No.	Description	Age (years BP)
Oldest Tundra Phase[12]		
W-93[10]	Poggenwisch, Holstein, northern Germany. Calcareous gyttja. Hamburgian II culture. Slightly later in Oldest Tundra than W-172.	15,150 ± 350
W-172[11]	Meiendorf, Holstein. Gyttja. Hamburgian I.	15,750 ± 800
ARCHAEOLOGICAL SITES		
Germany—Antler Series[12]		
W-264	Meiendorf, Holstein (see W-93). Hamburgian (Magdalenian).	11,870 ± 200 11,790 ± 200
W-271	Poggenwisch, Holstein (see W-172). Hamburgian (Magdalenian)	11,750 ± 200
W-261	Stellmoor, Holstein. Hamburgian (Magdalenian).	12,450 ± 200
W-266	Munzingen, near Freiburg. Magdalenian.	10,100 ± 250
W-269	Kneigrotte, Thuringen. Magdalenian.	8,800 ± 200
W-267	Petersfels, Baden-Wurttemberg. Magdalenian.	8,200 ± 200
Southern France		
C-577[14]	LaGarenne. Burned bone. Magdalenian.	11,109 ± 480
C-578[14]	LaGarenne. Charcoal and burned bone. Same horizon as C-577.	15,847 ± 1200
C-579[14]	LaGarenne. Burned bone, same horizon as C-577.	12,986 ± 560
C-406[16]	Lascaux Cave. Charcoal. Upper Perigordian or very early Magdalenian.[15]	15,516 ± 900
W-151[11]	Abri Pataud. Charcoal. Perigordian IV.	23,600 ± 800
W-191[11]	Abri Pataud. Same horizon as W-151.	24,000 ± 1000

(1) Anderson, Levi, and Tauber, 1953.
(2) Iversen, 1953
(3) Krog, 1954
(4) Straka, 1956
(5) Straka and DeVries, 1956
(6) Arnold and Libby, 1951
(7) Firbas, 1954a
(8) Godwin, 1951
(9) Firbas, Müller, and Münnich, 1955
(10) Suess, 1954
(11) Rubin and Suess, 1955
(12) Rubin and Suess, 1956
(13) Schütrumpf, 1955
(14) Libby, 1951
(15) Movius, 1951

Radiocarbon Laboratories

C — Chicago
GRO — Groningen
H — Heidelberg
K — Copenhagen
W — Washington

A distribution map (fig. 1) compiled by Gross shows Alleröd localities in Europe ranging from Russia, southern Norway, and Scotland in the north to Romania and southern France in the south. Its identification is apparently not difficult in the north close to the glacial border, where the climatic fluctuations were pronounced and where many of the pollen profiles have a base of known glacial correlation. In this region it has been widely identified in scores of profiles examined in the half-century since it was first demonstrated in Denmark by Hartz and Milthers. South from the glaciated and immediate periglacial regions, however, both of the above conditions useful for its identification are less favorable. The fluctuations of the Alpine ice cap had a limited effect on the climate and vegetation of southern Europe, and the correlations

of these fluctuations with those of the North European ice sheet have been subjects of disagreement. Although Gross does not discuss the problem, it is possible that some of the reported Alleröd occurrences beyond the regions of the Last Glaciation and its immediate periglacial area may actually represent an earlier (or later?) warm fluctuation (see below).

Important confirmation of pollen correlation of Alleröd beds in the periglacial region has come from the discovery of volcanic ash in the Alleröd horizon at 8 lacustrine bogs in central and southern Germany. The source of the ash is the Laacher volcanic region in the Eifel Mountains in the middle Rhine valley south of Bonn, 100-200 miles from the Alleröd sites in question. The bogs in the volcanic area itself show that the datable eruptions continued throughout the Younger Tundra phase and into the beginning of the Preboreal (Straka, 1956; Frechen and Straka, 1950). These bogs bottom in thick ash, however, that may date back to the Alleröd. It is possible that only the Alleröd eruptions broadcast their products to a great distance, so that over most of the periglacial area the ash may remain a useful key indicator for Alleröd time.

In northern Europe the Alleröd interstadial has long been correlated with the ice retreat prior to the construction of the late Gotiglacial Salpausselkä-Central Swedish moraines, for Alleröd development is found nowhere north of these moraines. The extent of ice recession during the Alleröd interval is not known. The succession of dates (12,000 to 10,800 years BP) determined at Copenhagen for the upper half of the series of Alleröd laminae at Ruds Vedby (Denmark) suggests that the interstadial endured for at least 1000 years (Iversen, 1953).

YOUNGER TUNDRA PHASE

The beginning of ice recession from the Central Swedish moraines marked the end of the Gotiglacial ice-retreat phase of the Late-Glacial and the beginning of the Finiglacial phase of the Post-Glacial (table 1). This event was dated as 7912 BC in the DeGeer (1940) varve chronology, or 9862 before 1950. This figure was later adjusted by Caldenius to 10,152 BP on the basis of relations of varves to the correlative Salpausselkä moraines studied by Sauramo in Finland.

In Denmark the beginning and end of the Younger Tundra phase are dated by radiocarbon samples from Bölling Lake as 10,770 and 10,300 BP respectively (Iversen, 1953). These dates bracket two determinations of the Younger Tundra zone at Schalkenmehren in the middle Rhine valley (10,770 and 10,550) (Straka, 1956), and are so close to the dates in the varve chronology that the work on the Swedish and Finnish varves by DeGeer, Liden, Sauramo, and others must be considered correct for the last 11,000 years.

THE BOLLING INTERSTADIAL AND OLDER TUNDRA PHASE

In pollen profiles in the former Bölling Lake in western Denmark, well outside the correlative of the Pomeranian moraine, Iversen discovered a brief increase of birch within the Older Tundra zone. This was interpreted as registering a warm fluctuation prior to the Alleröd, and the succession of pollen

zones have since been called Oldest Tundra, Bölling, Older Tundra, Alleröd, and Younger Tundra.

The Bölling phase has been identified at three localities in the Hamburg-Bremen-Lübeck area in adjacent Germany and at six localities in Holland (Gross, 1954, p. 194; 1955, p. 110). It has also been found beneath the ash-bearing Alleröd layer at Gaterslebener Lake near Aschersleben in central Germany. Still farther south in southwest Germany the Bölling is suggested by a pre-Alleröd birch expansion in pollen profiles, but in this area the climatic effects of minor fluctuations of the Scandinavian and Alpine ice sheets were only weakly recorded in the vegetation (Gross, 1954, p. 202).

The correlation of the Bölling interstadial with a retreat phase of the Scandinavian ice sheet has been discussed at some length by Gross (1954, 1955). At Heiligenhafen near Lübeck the Bölling occurs in a bog developed on the main Pomeranian moraine, and at the edge of Gaterslebener Lake the pollen-bearing sediments rest on the Youngest Loess, which Gross correlates with the Pomeranian. According to this view the Bölling must postdate the Pomeranian stadial (the last phase of the High-Glacial). The retreat from the Pomeranian moraine to the Langeland moraine along the Baltic coast defines the Daniglacial phase of the Late-Glacial;[2] it was marked by the formation of a broad zone of stagnant ice in northern Germany between the two morainic belts. In the ice-block lakes which soon formed in this zone were deposited sediments bearing subarctic fauna previously assigned to the "Masurian interstadial". Sediments of this type were locally overridden on the north by the Langeland ice advance. The climate during this time, however, was still sufficiently severe so that active solifluction and thawing of permafrost prevented orderly accumulation of pollen-bearing sediments, according to Gross. Gross believes that as far as the vegetation was concerned the important break in climate came rather in the retreat from the Langeland moraines (starting the Gotiglacial interval); pollen of the Oldest Tundra zone was then deposited undisturbed on top of the fossil-bearing fresh-water sediments, and the Bölling phase soon followed.

Many of these relations are still under study by various workers, however, and the glacial and periglacial sequence is not everywhere firmly related to the pollen stratigraphy in northern Germany and eastern Denmark. Gaps in the continuity of the various Pomeranian moraines, lack of stratigraphic sections, and disturbances by periglacial frost action seem to cause differences in interpretation.

[2] The term Daniglacial was first used by DeGeer for the interval of ice retreat across Denmark from moraines correlative with the Brandenburg moraine up to the Scanian moraines of southern Sweden, which he correlated in turn with the Pomeranian moraines; the term Gotiglacial was used for the interval from the Scanian to the Central Swedish moraines. The correlation of Scanian with Pomeranian has since been questioned, and Zeuner (1952, p. 31), in adopting the view that the Pomeranian is older than the Scanian, has confined the Daniglacial to the interval from Pomeranian to Scanian. Gross (1954) further confines the Daniglacial to the interval from the main Pomeranian to the North Pomeranian moraine (see table 1) and assigns to Gotiglacial the balance of the retreat to the Central Swedish moraines. Flint (1947, p. 333) and Deevey (1949, table 2), on the other hand, use the term Daniglacial for the first part of DeGeer's interval, i.e. the retreat from the Brandenburg to the Pomeranian moraine.

The Bölling fluctuation has been dated by radiocarbon analysis of samples collected from the deposits at the Gaterslebener Lake locality near Aschersleben east of the Harz Mountains in central Germany. This is well beyond the border of the last ice sheet and an ideal site because the later Alleröd fluctuation here is defined by volcanic ash (Müller, 1953). Two samples from the base of the Bölling zone were determined as 12,700 and 13,250 years old, and one from the lower part of the overlying Older Tundra zone as 12,300. On the lake border the basal peat of the Oldest Tundra phase is strongly disintegrated (by frost action?) and rests on the Youngest Loess, which is correlated with the Pomeranian stadial (Gross, 1954, 1955). The relatively young radiocarbon dates support Gross's correlation of the Bölling with the later Gotiglacial (post-Langeland) retreat rather than with the Daniglacial (post-Pomeranian pre-Langeland) retreat.

OLDEST TUNDRA PHASE

Prior to the Bölling zone the pollen profile shows higher percentages of non-arboreal pollen, decreased tree-pollen frequency, high content of willow and relatively low content of birch (Schütrumpf, 1955). The pollen-bearing sediments generally bottom in sand or clay that contain only scattered pollens secondarily transported or blown in from distant sources.

According to Gross, the Oldest Tundra phase terminated with the retreat of the ice from the Langeland moraine during the Bölling phase, as explained above. According to this concept, much of the early record of the Oldest Tundra phase during ice retreat from the Pomeranian to the Langeland moraine would have been destroyed by periglacial solifluction. Pertinent to the chronology of this interval is the pollen analysis and radiocarbon dating of Upper Paleolithic archeological sites in the Hamburg region. The Hamburgian I cultural stage at the site of Meiendorf is dated as 15,750 BP, and the Hamburgian II stage at nearby Poggenwisch as 15,150 BP. The pollen profiles at both sites have been studied by Schütrumpf (1955), who assigned the cultures to the Oldest Tundra phase, with the Hamburgian II site appropriately showing already the pollen changes pointing to the distant approach of the Bölling interstadial. Inasmuch as the Oldest Tundra and Bölling phases are identified in profiles at nearby Heiligenhafen on top of the main Pomeranian moraine (Gross, 1955, p. 111), we can extend the main Pomeranian back at least to 15,750 BP. At Grömitz near Lübeck on the Baltic coast (Gross, 1955, p. 111) Hamburgian II artifacts are deeply imbedded in till whose correlation with a somewhat later Pomeranian moraine is implied. This relation suggests that the Pomeranian (or at least the Daniglacial in Gross's sense) survived 15,150 BP, although Gross proposes that the burial of the artifacts may have resulted from solifluction rather than overriding by glacier ice.

Other radiocarbon dates of archeological sites in Europe have not as yet contributed much to the correlation problem. The Hamburgian culture is correlated with the Upper Paleolithic Magdalenian VIa, which has been found farther south at Schussenquelle also in the Oldest Tundra zone. At Andernach am Rhine, however, it appears in Alleröd beds with confirmatory Laacher

volcanic ash (thus about 11,500 BP). On the other hand, three different samples from a single Magdalenian layer at La Garenne in southern France were dated as 15,847, 12,986, and 11,109 BP, and charcoal from Upper Perigordian (or very old Magdalenian) at Lascaux Cave in the Dordogne of the same region as 15,516 BP. Perigordian IV, on the other hand, was dated as 24,000 and 23,600 at Abri Pataud in the Dordogne.

The anomalies among these dates for the Magdalenian of central Germany and southern France may be explained by appealing either (1) to local persistence of older cultures, (2) inherent errors in using Paleolithic cultures as index fossils even in nearby areas, or (3) inaccuracies in the sampling or in the C-14 dating. More analyses are needed for this time range, particularly at those archeological sites which can be related to the pollen stratigraphy or to the glacial sequence.

A test series of new radiocarbon analyses on unburned antlers from several Magdalenian sites in Germany has been released subsequent to Gross's discussions, but proved somewhat disappointing: the dates are consistenly younger than expected on the basis of the pollen chronology and the other C-14 dates. Pertinent Hamburgian dates are 11,790 and 11,870 for Meiendorf (dated as 15,150 from gyttja), 11,750 for Poggenwisch (dated as 15,750 from gyttja), and 12,450 for Stellmoor. Magdalenian sites in southern Germany yielded antler dates ranging from 10,100 down to 8,200 (table 2).

CORRELATION WITH THE ALPINE SEQUENCE

Correlation of the maximum and retreatal phases of the Weichsel glaciation of the Scandinavian ice sheet with those of the Würm glaciation in the Alps has never been completely satisfactory. Attempts at connection via the periglacial loesses and terraces of central Germany by Zeuner (1952) have been clouded by undue application of the radiation curve of inferred climatic fluctuations. The point has been reached, in fact, where Narr (1953), in view of the misuse of the terms Würm I, II, and III outside the Alps, recommends that a separate terminology be employed for the periglacial loesses and terraces, at least as far as archeologic dating is concerned.

Identification of the Alleröd layer in pollen profiles at many localities in southern Germany and in the Alpine piedmont again provides a key horizon for Late-Glacial correlation, and on the basis of many profiles Firbas (1949, 1950) has constructed forest maps of Europe for the Alleröd as well as for succeeding phases of the Late- and Post-Glacial. As mentioned above, the correlation of the Alleröd horizon in areas far removed from the margin of the Scandinavian ice sheet might seem to rest on a weak foundation because the age of the base of an analyzed bog may not be known and because vegetation is dynamic in its composition and migrations. Americans unaccustomed to the bulk and precision of European pollen analyses might sympathize with Deevey's earlier skepticism (1949, p. 1326): "It may be churlish to remark that there is no proof that the pollen spectra from which (Firbas' maps) are drawn are of exactly the same age." Firbas (1954b), however, has since specifically discussed the problem of synchronization of European pollen diagrams in some detail, and the increasing network of pollen profiles from

central and southern Europe presents an impressive picture, especially when they include analysis of the non-arboreal pollen and the tree-pollen frequency. The Alleröd correlations are confirmed at least for southern Germany by the fortunate occurrence of Laacher volcanic ash within the Alleröd layer at several localities. Radiocarbon dating of other Alleröd occurrences can be expected to support the general chronology.

Within the Alps, great hope was held for an independent absolute chronology of the Post-Glacial by Welten's careful pollen study of the varved gyttja of Faulensee Bog near Interlachen, Switzerland (Deevey, 1946). The bog is located on a moraine which Welton correlates with the Central-Swedish-Salpausselkä moraines, and the pollen-varve chronology places the beginning of the Post-Glacial (change from willow to birch) at about 8600 BP, compared to 10,800 for northern Europe. Zeuner (1952, p. 90; but *cf.* p. 155), however, has objected that the moraine on which the bog is located represents the Bühl stadial, correlated by him with the Pomeranian of the north, or at best (Gross, 1954) with the Langeland, rather than with the Salpausselkä. Such distant correlations of moraines must be considered largely as opinions. Gross further rejects Welten's chronology, however, on the basis of the fact that the Alleröd (ca. 11,500 BP) has been identified in Alpine valleys as high as 2100 m above sea level, indicating that the ice must have receded from the Faulensee site (590 m) long before 9600 BP, the date required by Welten. It might be pointed out, however, that if the chronology does in fact start at an earlier date, as Gross insists, the pollen profiles should reveal an Alleröd oscillation, and apparently they do not.

The identification of the Alleröd in the Alps confirms for Gross (1954, p. 201) the correlation of the "Final Glaciation" (Schlern, Gschnitz, and Daun stadials) with the Central Swedish moraines and the Younger Tundra phase, as had long ago been suggested by Penck. Gross correlates the next older stadial ("Bühl") of the Alps with the Langeland Moraine near the Baltic coast, and the moraines next downstream (Zürich-Singen-Olkofen) with the Pomeranian (see also Zeuner, 1952, p. 155). Despite glacial retreat from the last-named Alpine moraines far up the valleys to the Ammersee moraines, the climate apparently remained sufficiently severe in the Alpine piedmont for frost cracks to form in the Youngest Loess, and presumably the accompanying soilfluction caused destruction of incipient pollen-bearing deposits (Gross, 1954, p. 202). At least Gross selects this type of evidence to strengthen his correlations with northern Europe, where he had employed the same line of reasoning for the ice retreat from the Pomeranian to the Langeland moraines. Although such correlations based on loess may be questionable in detail, it may be noted that the pollen record shows a very slow advance of the forest up the deglaciated valleys, considering the high elevations to which the snow-line had retreated by this time (Firbas, 1950). The absence of protective forest cover during this interval would favor disturbance of the ground by frost action, and Gross's line of reasoning is thereby supported. Firbas suggests that forest migration may have been controlled by the length of growing

season; this would seem to imply that Alpine glaciers receded because of decreased winter nourishment rather than increased summer warmth.

Although pollen chronology has aided in the correlation of the Late-Glacial events of Northern Europe and the Alps, there remain internal problems for the earlier stages for both regions. For example, in contrast to the correlation presented by Gross (table 2), some of the Alpine geologists consider that the Zürich (Olkofen) moraines represent Würm I moraines that were later overridden by Würm II ice that terminated at the Killwangen-Schaffhausen moraines (Klebelsberg, 1949, p. 693-704). Upstream from these moraines of the Würm maximum (W-II) are in turn the moraines of the Schlieren stadial (Würm III), then the overridden Würm I (Zürich-Olkofen moraines), then the Ammersee ("Bühl") moraines mentioned above, and finally the triple succession of the "Final Glaciation" (Schlern, Gschnitz, and Daun). Klebelsberg does not offer to correlate the Würm stages beyond the Alps, and the question may be left open at least for the pre-Ammersee stadials. The stratigraphic position of various interstadial deposits reported in the Alps leaves the outsider confused (Ebers, 1955; Klebelsberg, 1949, p. 692-709), especially with the variable use of the terms Würm I, II, and III. Now even the relation of Riss to Würm is being challenged (Zeuner, 1954; Narr, 1953). Judson (Movius and Judson, 1956) has recently analysed a part of the problem with circumspection, but the correlations must still be considered fluid.

Here beyond the time range of effective pollen studies, and without as yet the aid of radiocarbon dates, correlations must depend largely on detailed studies of the glacial and periglacial stratigraphy, morphology, pedology, and paleontology, which in the long run are the more fundamental approaches. American workers must not discount the difficulties in intra-continental correlation, however, for it has been only recently that comprehensive studies of the younger glacial substages of the Rocky Mountains have permitted direct correlations with the late Wisconsin substages of the continental ice sheet (Horberg, 1954); earlier correlations by means of the loesses, buried soils, and terraces of the Great Plains have not been fully satisfactory. For the same time range in Europe, however, correlations are aided by pollen stratigraphy as well as radiocarbon dating, so the problem should soon be resolved.

The Riss-Würm complications in the Alps are matched in a sense in northern Europe by the position of the Warthe, which is now generally allied to the Saale (Woldstedt, 1950a, p. 359-363; 1950b; 1954; Von der Brelie, 1955) or at best considered as a separate stage (Klebelsberg, 1949, p. 630) rather than as the first sub-stage of the Last Glaciation, the view more familiar to American readers (Zeuner, 1952, p. 114; Deevey, 1949, p. 1323; Flint, 1947, p. 329). These problems are reminiscent of the Iowan-Illinoian controversy in America 25 years ago, and in fact resemble new difficulties that have arisen in the early Wisconsin in connection with the Tazewell, Iowan, Farmdale, and an unnamed drift in southern Ohio (Flint and Rubin, 1955). Just as radiocarbon dates have necessitated important revisions of the late Wisconsin chronolgy and are involved as well in early Wisconsin problems, so also in both northern Europe and the Alps the application of this technique may

settle some problems and create others, and eventually permit detailed trans-Atlantic correlations for the last glacial age. Reliable pollen chronology unfortunately would seem to start not before the Late-Glacial all over Europe. Its application to earlier interstadial or interglacial deposits has not been fully developed as yet (Von der Brelie, 1955).

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THE SYSTEM WATER—NEPHELINE—ALBITE: A THEORETICAL DISCUSSION

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ABSTRACT. At an invariant or quintuple point in a three-component system five pressure-temperature curves of univariant equilibria intersect. The sequence of these P-T curves, that is, the order in which they are met in either their stable portions or their metastable prolongations is determined by the compositions of the phases at that point. This proposition is proved, and its application is illustrated by a discussion of possible P-T curves and invariant points in the system water—nepheline—albite.

The following discussion has been written primarily as an illustration of the application of a powerful theoretical method in a field of physical chemistry in which there has been active and vigorous growth in recent years. The system chosen is one in which the author worked many years ago in an unsuccessful attempt to make jadeite (Yoder, 1950), a problem which has since been solved by the application of improved methods for the development of high pressure of water at high temperatures.

In studying systems in which water is one component, especially when a compound containing water, such as analcite ($Na_2O \cdot Al_2O_3 \cdot 4SiO_2 \cdot 2H_2O$), is formed, it is useful to consider the pressure-temperature, or P-T, curves of univariant equilibrium. These curves in a three-component system are projections of curves inside a four-dimensional hyperprism, of which the axes are pressure, temperature, and two composition variables, on to the pressure-temperature side. At an invariant point in a three-component system there are five phases, which can coexist only at the pressure and temperature of the invariant point. If either pressure or temperature is changed, one of these five phases must disappear, leaving a univariant system of four coexisting phases. Since any one of the five phases at the invariant point may disappear, there will be five P-T curves representing five different univariant equilibria proceeding from each invariant point.

This discussion is arbitrarily restricted to reactions in which analcite on heating under appropriate pressure conditions decomposes with formation of either nepheline plus albite, or jadeite. The conceivable formation of natrolite, of hydronepheline, or of quartz is not considered. The only phases to be considered are a gas, a liquid, analcite, nepheline ($Na_2O \cdot Al_2O_3 \cdot 2SiO_2$), jadeite ($Na_2O \cdot Al_2O_3 \cdot 4SiO_2$), and albite ($Na_2O \cdot Al_2O_3 \cdot 6SiO_2$). To discuss all possible phases it would be necessary to consider the quaternary system H_2O—Na_2O—Al_2O_3—SiO_2, shown in figure 1. Since the theoretical composition of each solid phase to be considered lies in that section of the tetrahedron defined by a plane through the corners H_2O and SiO_2 and the point $Na_2O \cdot Al_2O_3$ on the side Na_2O—Al_2O_3, the equilibria under discussion can be considered as ternary, and represented by the triangle H_2O—$Na_2O \cdot Al_2O_3$—SiO_2, provided that the gas and liquid phases also lie in this triangle. For the purpose of discussion it is convenient to consider that the gas is pure water. Morey and Hesselgesser (1951) found that the gas phase formed by passing steam superheated to 500° C over albite at low pressure resulted in decomposition of the albite, but at high pressure the albite appeared to be dissolved as such. At 400 bars water pressure the amount of material dissolved by the superheated steam amounted

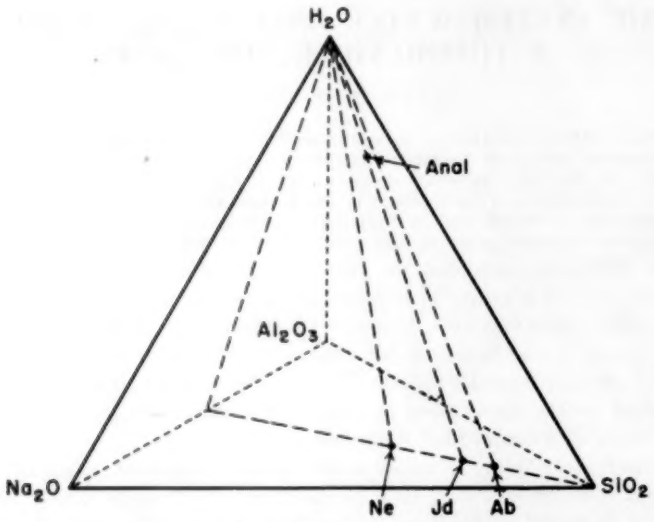

Fig. 1. The system H_2O—Na_2O—Al_2O_3—SiO_2, showing the plane through H_2O, SiO_2, and compounds having a ratio of Na_2O:Al_2O_3 of 1:1.

to only 0.006 weight percent, and the molecular ratio of this dissolved material was 1.41:1.0:12.2. However, at 2000 bars steam pressure, 0.27 percent of material was dissolved, and the molecular ratio was that of albite, 1:1:6, within experimental error. At high pressures, albite is congruently soluble in steam. No experimental results are available for nepheline or jadeite, but it is not unreasonable to assume that with them also at high pressure the gas composition will be in the plane H_2O—$Na_2O \cdot Al_2O_3$—SiO_2 near the H_2O apex. If the gas were to contain, for example, more Na_2O than corresponds to this plane the system could not be considered ternary but would be quaternary, and at equilibrium there would be one more phase. However, if the amount of solid material dissolved is small, it may not be possible to detect experimentally a small deviation of the gas composition from the assumed plane.

The discussion can be further simplified by considering as components the compositions H_2O, $Na_2O \cdot Al_2O_3 \cdot 2SiO_2$, and $Na_2O \cdot Al_2O_3 \cdot 6SiO_2$. These compositions will be indicated by Ne and Ab, but with the essential condition that these symbols represent the indicated compositions, not phases. The names nepheline and albite mean minerals which rarely have the ideal chemical composition and which have definite physical properties. In the course of this discussion Ne and Ab are used primarily to indicate components of definite chemical composition without implication of physical properties; when used in the sense of crystalline phases there should be no confusion. Accordingly, we shall consider the ternary system H_2O—$Na_2O \cdot Al_2O_3 \cdot 2SiO_2$—$Na_2O \cdot Al_2O_3 \cdot 6SiO_2$ and designate these components by the symbols G, Ne, and Ab, respectively.

We shall first assume that there is a quintuple point at which the phases are G (H_2O), L (liquid), A (analcite), Ne (nepheline) and Ab (albite), and

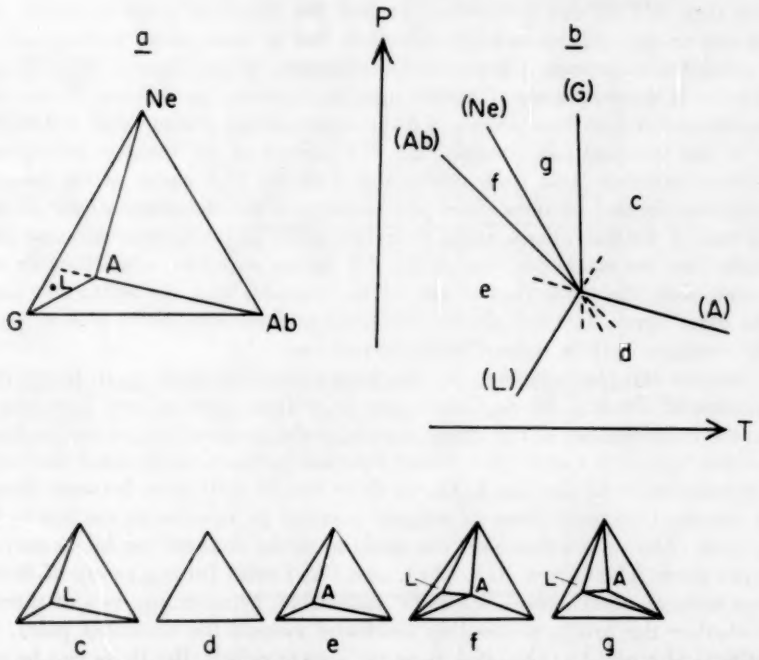

Fig. 2. The sequence of P-T curves around the quintuple point gas-liquid-nepheline-albite, when the liquid composition is in the triangle G-Ne-A, between G and the prolongation of the line Ab-A.

that a liquid is formed before jadeite makes its appearance. Whether or not such a quintuple point is capable of stable existence can only be determined by experiment. Assume first that the composition of the liquid is in the small triangle formed by G, A, and the prolongation of the line Ab-A, as shown in figure 2a. There will be five univariant P-T curves proceeding from this invariant point, each one obtained by the disappearance of a different one of the five phases. They will be

(G)	$A = L + Ne + Ab$
(L)	$A = G + Ne + Ab$
(A)	$G + Ne + Ab = L$
(Ne)	$G + A = L + Ab$
(Ab)	$G + A + Ne = L$

in which each univariant system is designated by the symbol in parentheses of the phase which has disappeared. The P-T curve (G) is that of a system in which all the phases are liquid or solid, there will be but little volume change in the reaction, and hence the curve will be almost vertical. The equations which determine the slopes of these curves will be discussed subsequently. The curve (L) is that of the reaction

$$A = G + Ne + Ab$$

and will go from the invariant point to lower pressure and temperature. The sequence of the P-T curves around the invariant point, that is, the order in

which they will be met proceeding around the invariant point in either the clockwise or the counterclockwise direction, can be deduced by making use of the coincidence theorem (Morey and Williamson, 1918; Morey, 1922, 1936) which for a three-component system may be expressed as follows: When the compositions of any three phases in a three-component system lie on a straight line in the composition triangle, the P-T curves of all ternary univariant equilibria coincide with each other, and with the P-T curve of the binary equilibrium formed by these three phases alone. When the compositions of the other two of the five phases at the invariant point lie on opposite sides of this straight line, the stable portions of the P-T curves coincide; when they lie on the same side, the stable part of one curve coincides with the metastable part of the other curve. The two phases not on the straight line, which play no part in the reaction, may be termed indifferent phases.

Assume the phase L (fig. 2a) to change composition so as to be on the projection of the line Ab-A. This it can do without crossing any line which joins the compositions of two other phases, or the prolongation of such a line. Then the curves (G) and (Ne) would coincide stable to stable since they are on opposite sides of the line L-Ab, so there can be no curves between them. Now assume L to move from its original position so as to be on the line G-A. (Ne) and (Ab) would then coincide stable to stable, so there can be no curves between them. The curves (G), (Ne), and (Ab) must form a group of three curves without other curves, stable or metastable, between any two of them; but whether the order, proceeding clockwise around the invariant point, is (G) (Ne) (Ab) or (Ab) (Ne) (G) is as yet undetermined. But there can be no curves between the metastable and stable parts of (G) and (L), because phase A can be considered as moving to the line Ne-Ab without crossing any straight line passing through the compositions of other phases. Hence the sequence of P-T curves must be as shown in figure 2b. It is to be emphasized that this sequence is diagrammatic, and the curves (Ne) and (Ab) may be in any position between (G) and the metastable prolongation of (A), and (A) may have any position between the metastable prolongations of (L) and (Ab).

The equations for the univariant equilibria of figure 2b may be derived as follows. For each phase there is an equation of the form of Gibbs 97, which, when composition is expressed in mole fractions, becomes for the gas

$$V^v\,dP = S^v\,dT + (1 - X - Y)\,d\mu_1 + X\,d\mu_2 + Y\,d\mu_3$$

in which V and S represent the volume and entropy of one mole of the mixture, μ_1, μ_2, and μ_3 the molar chemical potentials of the components whose mole fractions are given by $(1 - X - Y)$, X, and Y. The component represented by $(1 - X - Y)$ is usually the most volatile component, in this case water, and is placed in the lower lefthand corner of the component triangle. Since there are four phases in a univariant equilibrium in a three-component system, there are four equations of the form of Gibbs 97, one for each of the four coexisting phases, and from these four equations any three of the intensive variables P, T, μ_1, μ_2, and μ_3 can be eliminated by the familiar process of cross-multiplication. This elimination is performed more easily by making use of determinants, which consists in writing down the coefficients in a formalized manner, and operating on them according to some simple rules.

For example, for the equilibrium (Ab), which is the reaction

$$G + A + Ne = L$$

the determinants obtained by the elimination of $d\mu_1$, $d\mu_2$, and $d\mu_3$ are:

$$\frac{dP}{dT} = \frac{\begin{vmatrix} S^G & 1 - X^G - Y^G & X^G & Y^G \\ S^L & 1 - X^L - Y^L & X^L & Y^L \\ S^{Ne} & 1 - X^{Ne} - Y^{Ne} & X^{Ne} & Y^{Ne} \\ S^A & 1 - X^A - Y^A & X^A & Y^A \end{vmatrix}}{\begin{vmatrix} V^G & 1 - X^G - Y^G & X^G & Y^G \\ V^L & 1 - X^L - Y^L & X^L & Y^L \\ V^{Ne} & 1 - X^{Ne} - Y^{Ne} & X^{Ne} & Y^{Ne} \\ V^A & 1 - X^A - Y^A & X^A & Y^A \end{vmatrix}}$$

A fundamental property of determinants is that adding or subtracting a row or column from another row or column does not affect the value of the determinant. If we add columns 3 and 4 to column 2, we obtain

$$\frac{dP}{dT} = \frac{\begin{vmatrix} S^G & 1 & X^G & Y^G \\ S^L & 1 & X^L & Y^L \\ S^{Ne} & 1 & X^{Ne} & Y^{Ne} \\ S^A & 1 & X^A & Y^A \end{vmatrix}}{\begin{vmatrix} V^G & 1 & X^G & Y^G \\ V^L & 1 & X^L & Y^L \\ V^{Ne} & 1 & X^{Ne} & Y^{Ne} \\ V^A & 1 & X^A & Y^A \end{vmatrix}}$$

A common way to expand a determinant is by repeated expansion of the minors. The minor of the leading term, S^G, is the determinant

$$\begin{vmatrix} 1 & X^L & Y^L \\ 1 & X^{Ne} & Y^{Ne} \\ 1 & X^A & Y^A \end{vmatrix}$$

The entire determinant is expanded in this manner, and when the number of interchanges of rows is even the term is positive, when odd, negative. The expansion thus becomes

$$\frac{dP}{dT} = \frac{S^G \begin{vmatrix} 1 & X^L & Y^L \\ 1 & X^{Ne} & Y^{Ne} \\ 1 & X^A & Y^A \end{vmatrix} - S^L \begin{vmatrix} 1 & X^G & Y^G \\ 1 & X^{Ne} & Y^{Ne} \\ 1 & X^A & Y^A \end{vmatrix} + S^{Ne} \begin{vmatrix} 1 & X^G & Y^G \\ 1 & X^L & Y^L \\ 1 & X^A & Y^A \end{vmatrix} - S^A \begin{vmatrix} 1 & X^G & Y^G \\ 1 & X^L & Y^L \\ 1 & X^{Ne} & Y^{Ne} \end{vmatrix}}{V^G \begin{vmatrix} 1 & X^L & Y^L \\ 1 & X^{Ne} & Y^{Ne} \\ 1 & X^A & Y^A \end{vmatrix} - V^L \begin{vmatrix} 1 & X^G & Y^G \\ 1 & X^{Ne} & Y^{Ne} \\ 1 & X^A & Y^A \end{vmatrix} + V^{Ne} \begin{vmatrix} 1 & X^G & Y^G \\ 1 & X^L & Y^L \\ 1 & X^A & Y^A \end{vmatrix} - V^A \begin{vmatrix} 1 & X^G & Y^G \\ 1 & X^L & Y^L \\ 1 & X^{Ne} & Y^{Ne} \end{vmatrix}}$$

These determinantal composition coefficients represent areas of triangles. These areas are, by convention, positive when circumscribed counter-clockwise, negative when circumscribed clockwise. In figure 2a, the area,

$$\begin{vmatrix} 1 & X^L & Y^h \\ 1 & X^{Ne} & Y^{Ne} \\ 1 & X^A & Y^A \end{vmatrix}$$

which may be represented by A^{LNeA}, is negative, the area A^{GNeA} is negative, and the area A^{GLA} is negative. Area A^{GLNe} is positive, but it also may be made negative by changing the direction in which it is circumscribed from GLNe to GNeL. Since these are the same areas in numerator and denominator, each may be multiplied by –1, and the equation becomes

$$\frac{dP}{dT} = \frac{S^G A^{LNeA} - S^L A^{GNeA} + S^{Ne} A^{GLA} - S^A A^{GNeL}}{V^G A^{LNeA} - V^L A^{GNeA} + V^{Ne} A^{GLA} - V^A A^{GNeL}}$$

Since $A^{GNeA} = A^{LNeA} + A^{GLNe} + A^{GLA}$
the term $-S^L A^{GNeA}$ can be replaced by the terms $-S^L A^{LNeA} - S^L A^{GLNe} - S^L A^{GLA}$. Making these substitutions,

$$\frac{dP}{dT} = \frac{(S^G - S^L) A^{LNeA} + (S^{Ne} - S^L) A^{GLA} - (S^A - S^L) A^{GNeL}}{(V^G - V^L) A^{LNeA} + (V^{Ne} - V^L) A^{GLA} - (V^A - V^L) A^{GNeL}},$$

or dividing through by A^{LNeA},

$$\frac{dP}{dT} = \frac{(S^G - S^L) + (S^{Ne} - S^L) \frac{A^{GLA}}{A^{LNeA}} - (S^s - S^L) \frac{A^{GNeL}}{A^{LNeA}}}{(V^G - V^L) + (V^{Ne} - V^L) \frac{A^{GLA}}{A^{LNeA}} - (V^A - V^L) \frac{A^{GNeL}}{A^{LNeA}}}$$

All the areas are now positive, so that the area ratios are all positive. As figure 2a is drawn, A^{GNeL} is largest, A^{LNeA} next, and A^{GLA} smallest, so the ratios are all positive fractions. The entropy difference $(S^G - S^L)$ is positive, since it always requires heat to vaporize a liquid, and the differences $(S^{Ne} - S^L)$ and $(S^A - S^L)$ are negative, since it always requires heat to melt a solid. The difference between the second and third terms may be either positive or negative, but is necessarily small, and the entire numerator is certainly positive. The first term in the denominator will always predominate, so dP/dT is necessarily positive.

These areas can be calculated from the determinants. If the components are H_2O, Ne ($Na_2O \cdot Al_2O_3 \cdot 2SiO_2$), and Ab ($Na_2O \cdot Al_2O_3 \cdot 6SiO_2$), the composition of analcite in mole fractions is (0.666, 0.167, 0.167). Assume the liquid to be 0.75, 0.15, 0.10. Then

$$A^{LNeA} = \begin{vmatrix} 1 & 0.15 & 0.10 \\ 1 & 1 & 0 \\ 1 & 0.167 & 0.167 \end{vmatrix} = 0.05835$$

$$A^{GLA} = \begin{vmatrix} 1 & 0 & 0 \\ 1 & 0.15 & 0.10 \\ 1 & 0.167 & 0.167 \end{vmatrix} = 0.00835$$

$$A^{GNeL} = \begin{vmatrix} 1 & 0 & 0 \\ 1 & 1 & 0 \\ 1 & 0.15 & 0.10 \end{vmatrix} = 0.10$$

and the ratio

$$\frac{A^{GLA}}{A^{GNeL}} = \frac{0.00835}{0.05830} = 0.1431$$

and

$$\frac{A^{GXeA}}{A^{LNeA}} = \frac{0.10}{0.05835} = 1.714$$

The equation then becomes

$$\frac{dP}{dT} = \frac{(S^G - S^L) + 0.1431(S^{Ne} - S^L) - 1.714(S^A - S^L)}{(V^G - V^L) + 0.1431(V^{Ne} - V^L) - 1.714(V^A - V^L)}$$

Since the invariant point is the projection on the pressure-temperature side of a four-dimensional hyperprism in which the axes are pressure, P, temperature, T, and the two composition variables, X and Y, every point of the P-T diagram must represent uniquely the entire composition range of the phases present at the invariant point. The invariant point is the projection of a point within the hyperprism, and the several P-T curves representing univariant equilibria may radiate from the invariant point in any direction within the hyperprism. Along each of them not only pressure and temperature, but also the composition variables X and Y may change (see the discussion of figure 9).

The various univariant equilibria which radiate from the invariant point are obtained by assuming each in turn of the phases at the invariant point to disappear. If two phases disappear, for example, if one of the phases of a univariant equilibrium disappears, a divariant region is entered, and between each pair of P-T curves is one or more divariant regions. It has just been shown, however, that each point of every region must represent the entire composition range of the phases at the invariant point, hence the arrangement of divariant regions must be in harmony with this requirement. The distribution of divariant regions between the P-T curves is indicated by letters in figure 2b, referring to the smaller triangles figure 2c-g, which show how in each case the divariant regions occupy the entire triangle. The regions shown in these triangles may be deduced in several ways, but the most convenient method may be as follows. Start with curve (L) and proceed in a clockwise manner around the invariant point. Between (L), or A = G + Ne + Ab, and (Ab), or G + A + Ne = L, is a divariant region in which neither L nor Ab is present, the region (LAb), or G + A + Ne. This region between (L) and (Ab) is indicated in figure 2b by the letter e, and in figure 2e are the corresponding phase triangles, including G + A + Ne. These three phases are reacting phases in both the equilibria (L) and (Ab). This region is entered from (L) by all the albite being consumed in the reaction, and from (Ab) by all the liquid disappearing. Between (L) and (Ne) is the region (LNe), or G + A + Ab, which extends over the P-T curve (Ab). Whenever a region extends over a P-T curve that region can play no part in the reaction taking place along that curve. Thus (Ab) is the P-T curve of the reaction G + A + Ne = L, and the region G + A + Ab may be termed an indifferent region with respect to the reaction (Ab).

Between (L) and (G) is the region (LG), or A + Ne + Ab, which crosses over the curves (Ab) and (Ne). The region (LG) is an indifferent region in both (Ab) and (Ne). It is not possible to have a region extending from (L) over (G) to (A), because (L) would then cross its own metastable prolongation into a region in which it is by hypothesis unstable. These three divariant regions shown in figure 2e necessarily comprise the entire composition triangle. The other divariant regions can be determined in a similar manner.

Another method of determining the divariant regions is as follows. The reaction along (L) is

$$A = G + Ne + Ab,$$

and on continued reaction any one of these reacting phases may disappear. This gives the following four divariant regions: G + A + Ne, G + A + Ab, Ab + Ne + A, or G + Ne + Ab. The first three regions must be on one side of the curve, since A is found only on one side of the reaction, and the region G + Ne + Ab must be on the other side of (L). The first three regions are the ones found in figure 2e, the other single region in figure 2d. The reaction at (Ab) is G + A + Ne = L. Liquid can exist only to the right of this curve. To the right are the regions G + L + A, G + L + Ne, and L + A + Ne (fig. 2f), and also the regions G + A + Ab and A + Ne + Ab, both of which contain albite, extend over the curve (Ab), and are indifferent regions. They are both found in figure 2e, in which is also the region G + A + Ne, which is on the left side of reaction (Ab).

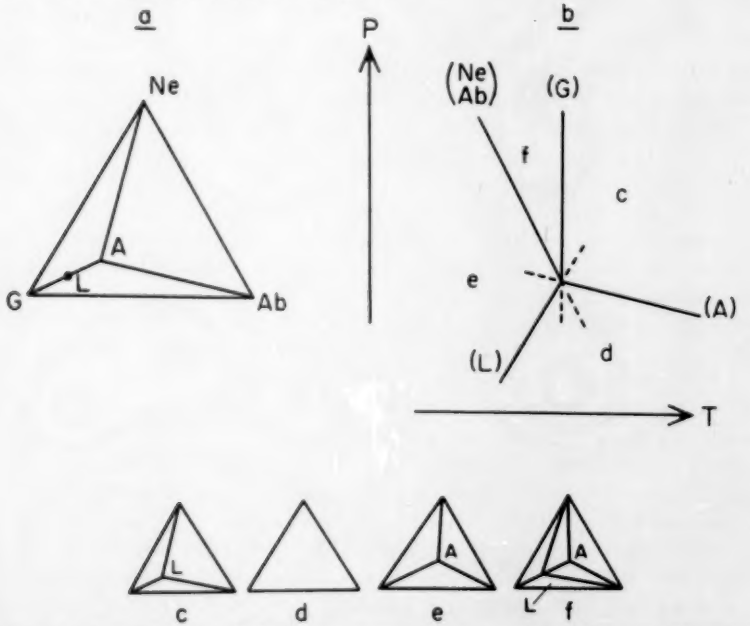

Fig. 3. The sequence of P-T curves around the quintuple point gas-liquid-nepheline-albite, when the liquid composition is between gas and analcite.

If the composition of the liquid were to change until it lies on the line G-A, the curves (Ne) and (Ab) would coincide stably with each other and with the P-T curve of the reaction G + A = L. Nepheline and albite are now indifferent phases. There are now (fig. 3b) only four P-T curves, four angles between them, and four possible distributions of divariant fields. At low temperatures and pressures, in the angle between (L) and (Ne)(Ab), figure 3e, the divariant fields are (LAb), or G + A + Ne, (LNe), or G + A + Ab, and (LG), or A + Ne + Ab. The reaction (L) is G + Ne + Ab = A. If there is not enough water, the gas will all be consumed in making analcite from nepheline and albite, and the resulting divariant region will be A + Ne + Ab. If there is enough water the reaction will proceed until either Ne or Ab is used up, leaving either G + A + Ab or G + A + Ne.

If any of the mixture of phases of figure 3e is compressed, the curve (Ne)(Ab) will be met, at which the reaction is G + L = A. If there is not enough water to complete this reaction, the region entered (fig. 3f) will be A + Ne + Ab. If there is enough water to form a liquid, the region will be either L + A + Ne or L + A + Ab, depending on whether nepheline or albite is in excess. With still more water, the region entered will be either G + L + Ne or G + L + Ab.

The equation of the slope of the curve (Ab) was found to be

$$\frac{dP}{dT} = \frac{(S^G - S^L) + (S^{Ne} - S^L)\frac{A^{GLA}}{A^{LNeA}} - (S^A - S^L)\frac{A^{GNeL}}{A^{LNeA}}}{(V^G - V^L) + (V^{Ne} - V^L)\frac{A^{GLA}}{A^{LNeA}} - (V^A - V^L)\frac{A^{GNeL}}{A^{LNeA}}}$$

When L falls on the line G-A, the area of the triangle G-L-A becomes zero, and the middle term drops out. The equation then becomes

$$\frac{dP}{dT} = \frac{(S^G - S^L) + \frac{X^G - X^L}{X^L - X^A}(S^A - S^L)}{(V^G - V^L) + \frac{X^G - X^L}{X^L - X^A}(V^A - V^L)}$$

which is the equation of the univariant three-phase curve A = G + L in the binary system water—analcite.

Return now to a mixture in the angle between (Ne)(Ab) and (L), e in figure 3b, and assume it is heated at a constant pressure below that of the invariant point. The reaction at the curve (L) is A = G + Ne + Ab and beyond (L) the only possible assemblages of phases is G + Ne + Ab (fig. 3d). On heating the analcite decomposes into G + Ne + Ab, and each of the divariant fields of figure 3d passes into the single field of figure 3d. The other possible phase reactions are easily deduced in a similar manner.

The phase L can be considered as moving across the line G-A into the triangle G-A-Ab. This will result in the continued movement of the P-T curve (Ne) across (Ab), so that the sequence in the group of three curves becomes (Ne) (Ab) (G).

Now consider that the phase L, originally in the triangle G-Ne-A, (fig. 2a) and on the gas side of the prolongation of the line Ab-A, first falls on this

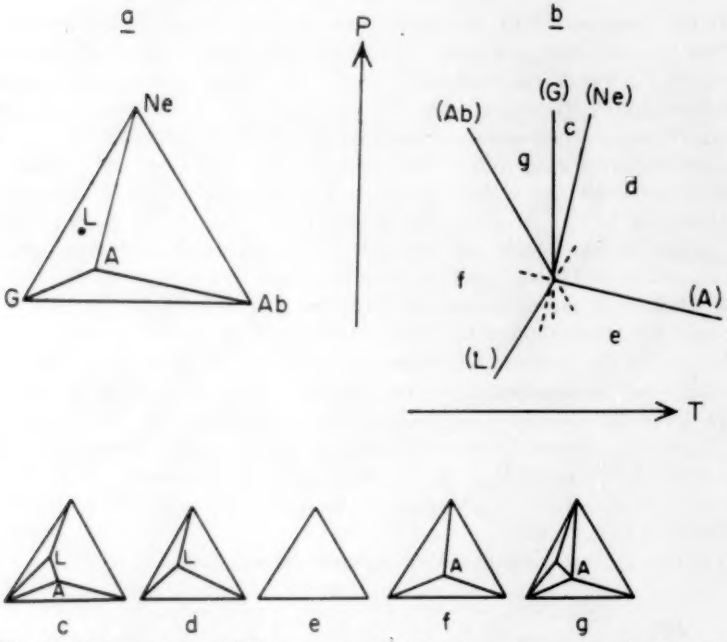

Fig. 4. The sequence of P-T curves around the quintuple point gas-liquid-nepheline-albite, when the liquid composition is in the triangle G-Ne-A, between Ne and the prolongation of the line Ab-A.

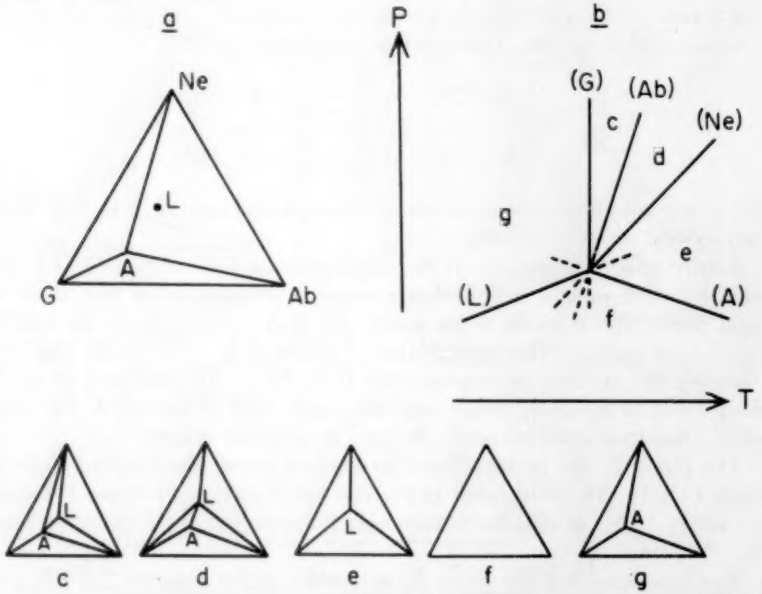

Fig. 5. The sequence of P-T curves around the quintuple point gas-liquid-nepheline-albite, when the liquid composition is in the triangle A-Ne-Ab, above the prolongation of the line G-A.

line, then crosses it. When it is on the line, the curves (G) and (Ne) coincide stably, and when it crosses the line they have interchanged positions. The composition relations now are those of figure 4a, the sequence of P-T curves as given in figure 4b, and the divariant fields as shown in figure 4c-g. Now suppose the liquid composition first falls on, then crosses the line A-Ne. When it lies on that line the curves (G) and (Ab) coincide; when it crosses that line they interchange positions. The order now has become (G) (Ab) (Ne). The compositions, P-T curves, and divariant fields are as shown in figure 5, and require no further discussion.

If liquid moves onto the prolongation of the line G-A it indicates a congruent melting of analcite, an extension of the binary equilibrium G + L + A to the quintuple point, where it ceases to be binary because of formation of nepheline and albite. The P-T curves (Ne), or G + L + A + Ab and (Ab), or G + A + L + Ne, coincide in their stable portions, since they are on opposites sides of the line G-L-A. They also coincide with the binary P-T curve A = G + L. This curve will be considered further in the discussion of figure 9.

Analcite is not stable in the region of figure 6e, which is between (L) and (A), and it should dissociate under these conditions. The curve (L) is

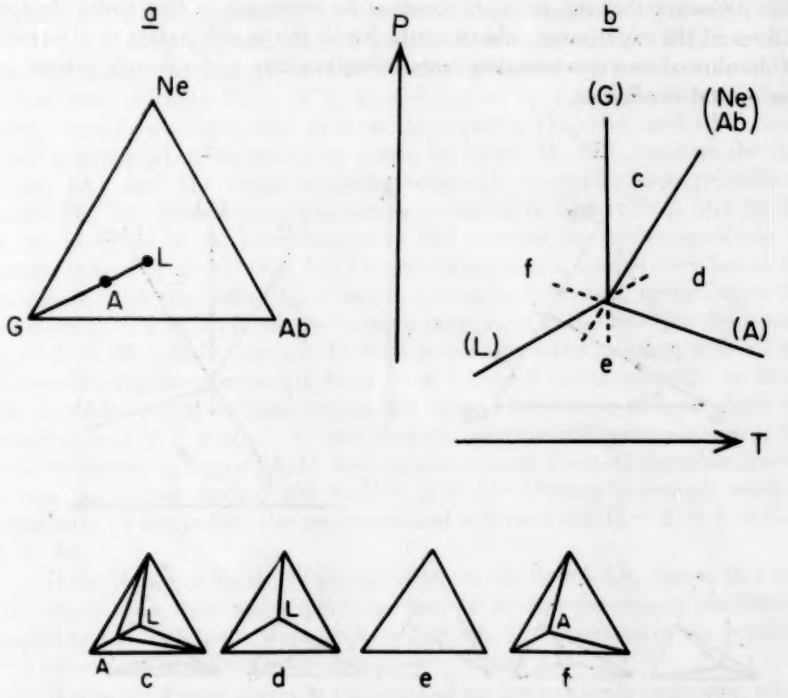

Fig. 6. The sequence of P-T curves around the quintuple point gas-liquid-nepheline-albite, when the liquid composition is in the triangle A-Ne-Ab, and on the prolongation of the line G-A.

the dissociation pressure curve of analcite, A = G + Ne + Ab, and if analcite in any of the regions of figure 6f is heated, on meeting curve (L) it decomposes according to the above reaction. The stable regions in figure 6f are A + Ne + Ab, G + A + Ab, and G + A + Ne, or in the binary system, analcite alone. If analcite is in the region of figure 6e, at a pressure below the dissociation pressure it should decompose, if the reaction is not prevented by passive resistance to change. If a break is found on a heating curve obtained in this region it merely means that the rate of decomposition has become rapid enough to cause an appreciable absorption of heat; it is not a point on an equilibrium curve. If analcite is heated at a pressure above the dissociation pressure curve, that is, above (L) but below the pressure of the invariant point, it is stable until it reaches the curve (L). It then should completely decompose, giving a strong heat effect; and if the resulting assemblages of phases, G + Ne + Ab, is cooled at the same pressure the reverse reaction should take place with formation of analcite and evolution of heat. At pressures and temperatures near the invariant point these reactions take place fairly readily, but they do not take place at low pressures and temperatures, under which conditions the P-T curve of the above reaction is difficult to determine accurately. For breaks found on heating curves to refer to equilibrium reactions it is necessary that the reaction observed be reversible in fact under the conditions of the experiment, otherwise the break found only refers to a measure of the rate of an experimentally irreversible reaction under poorly defined experimental conditions.

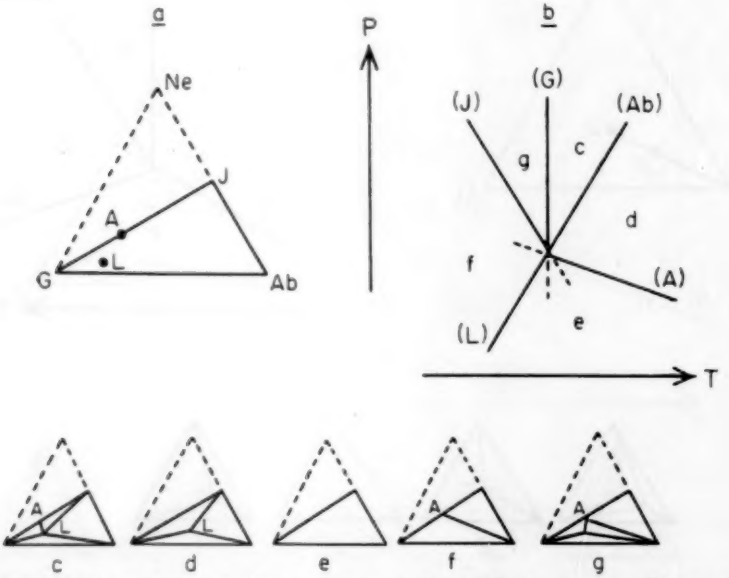

Fig. 7. The sequence of P-T curves around the quintuple point gas-liquid-analcite-jadeite-albite, in which the liquid composition is in the triangle G-A-Ab.

The preceding discussion has assumed that jadeite, J, is not formed. If there is a quintuple point at which both liquid and jadeite are phases, as well as gas and analcite, either nepheline or albite can be the fifth phase. Since five phases give an invariant point in a three-component system, it is not possible for the six phases to coexist in equilibrium, and the line G-J may be regarded as dividing the system into two independent ternary systems, G + Ne + J, and G + J + Ab, in which are formed the quintuple points G + L + A + Ne + J and G + L + A + J + Ab. It is assumed that both G and L are in the plane G-Ne-Ab, otherwise the entire quaternary system H_2O—Na_2O—Al_2O_3—SiO_2 must be considered.

Consider the phase assemblage of figure 7a, in which the liquid is in the triangle G-J-Ab. The phases present at the quintuple point will be G, L, A, J, and Ab, and normally there would be five P-T curves proceeding from it. But since G, A, and J are on a straight line, all P-T curves containing these phases will coincide with each other and with the binary P-T curve A = G + J. These curves are (L) and (Ab), and since they are on the same side of the line G-J they will coincide stable to metastable. As before, assume the P-T curve of the system (G) to be practically vertical, because it contains only liquid and solid phases, and the P-T curve of the equilibrium (L) to have a positive slope and to go to lower temperatures and pressures from the invariant point. Then its metastable extension above invariant point will be the curve (Ab), since (L) and (Ab) coincide stable to metastable. If L moved to the line A-Ab, (G) and (J) would coincide in their stable parts, so there can be no curve between them. If L, A, and J were on a straight line, (G) and (Ab) would coincide stably, so these three curves (J), (G), and (Ab) must form a group of three curves as drawn in figure 7b. If L were on the line G-Ab, (A) and (J) would coincide metastable to stable, as is possible in figure 7b. The divariant regions are as indicated in figures 7c-g, and by the letters in figure 7b. At low temperature and pressure the stable assemblage of phases is G + J + Ab (fig. 7e). On compression at a temperature below the invariant point the curve (L) is met and analcite is formed, according to the reaction G + J = A. If all the water is consumed in the reaction the region A + J + Ab will be entered. If there is enough water to unite with all the jadeite the region entered will be G + A + Ab. If the temperature is above the invariant point, on compression the curve (A) will be met, at which the reaction is G + J + Ab = L, and then the mixture will pass into one of the regions shown in figure 7d. If there is not enough water to complete the reaction, the region entered will be L + J + Ab; if there is enough water to react with all the jadeite the region entered will be either G + L + J or G + L + Ab.

If the liquid in figure 7a moves to lie on the line A-Ab, curves (G) and (J) coincide in their stable portions, and on further movement interchange positions as L enters the triangle A + J + Ab. The positions of the resulting P-T curves and divariant fields are shown in figure 8.

If now the liquid moves to the line G-J the system becomes binary, albite is an indifferent phase, and analcite has a congruent melting point. The invariant or quadruple point is a eutectic,[1] and the coexisting phases are G, L,

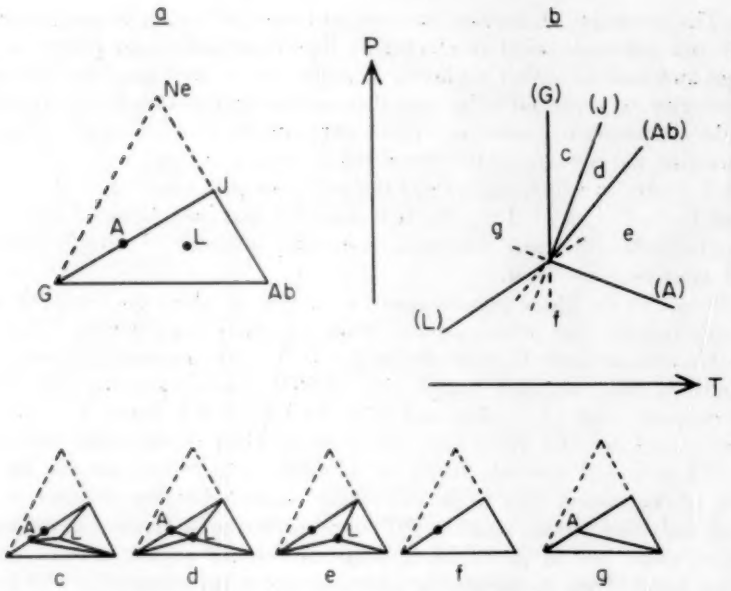

Fig. 8. The sequence of P-T curves around the quintuple point gas-liquid-analcite-jadeite-albite, in which the liquid composition is in the triangle A-J-Ab.

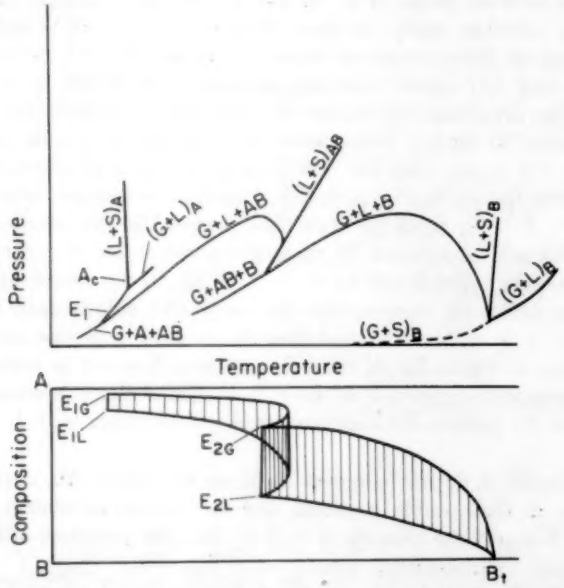

Fig. 9. Projections of a diagrammatic pressure-temperature-composition model of a system containing a volatile component, A, and a non-volatile component, B, which form a compound, AB, having a congruent melting point.

A, and J. The general relations in such a system are shown in figures 9a and 9b, in which are given two projections of the solid pressure-temperature-composition, or P-T-X, model. These figures are diagrammatic, with components A and B instead of water and jadeite and the compound is represented as AB, instead of analcite. Figure 9a is the projection of the solid model on the pressure-temperature side, and shows the various P-T curves. Figure 9b is the projection on the temperature-composition, or T-X, base, and shows the change in composition of the various phases with temperature. A_t is the triple point of A, and from it in figure 9a proceed four P-T curves, three of them unary, the fourth binary. The curve A-L_A gives the change of melting point with pressure and extends upward indefinitely, unless terminated by a triple point at which a new solid phase appears. The curve G-L_A is the vapor pressure curve of A, and terminates at the critical point A_c. The third unary curve, the vapor pressure curve of solid A, is not shown. The binary curve is the curve A_t-E_1, which terminates at the eutectic E_1 where the solid phase AB appears in equilibrium with gas and liquid. In figure 9b proceeding from A_t are shown the two curves A_t-E_1L and A_t-E_1G, which give the composition of the liquid with which solid A is in equilibrium and the gas coexisting with it. For greater clarity the content of component B in the gas in this diagram is assumed to be much greater than will be the case in any of the systems of the type under consideration. With most water-salt systems the gas is essentially pure water, and the curve A_t-E_1 in figure 9a coincides with the vapor pressure curve of ice.

From E_1 will proceed four P-T curves in figure 9a. The curve G + AB + B, shown in figure 9a goes to lower temperature and pressure. The curve L + AB + B, not shown in figure 9a, goes to higher pressures, and to either higher or lower temperature depending on the sign of the volume change in the reaction. Neither of these curves is shown in figure 9b, but neither the gas of the first equilibrium nor the liquid of the second will change rapidly. Also proceeding from E_1 are the curves G + L + A, already discussed, and the curve G + L + AB, the solubility or melting point curve of the compound AB, which has a point of maximum pressure, then one of maximum temperature, and terminates at the eutectic E_2, at which the P-T curve has a horizontal tangent. The negative second term then becomes preponderant and the P-T curve has a negative slope.

As the composition of the liquid comes nearer to the composition of the solid the terms in the denominator of the equation must be considered. In the usual case, $(V^{AB} - V^{L})$ is negative and much smaller than the positive difference $(V^{G} - V^{L})$, and that is true at the composition which causes the numerator to become zero. Beyond this, however, the difference $(X^{L} - X^{AB})$ becomes very small, the coefficient of $(V^{AB} - V^{L})$ becomes very large, the denominator becomes zero, and the P-T curve has a vertical tangent. Beyond this point the denominator becomes negative, and since the numerator is negative, the P-T curve again has a positive slope after passing through a point of maximum temperature.

[1] An invariant point is called a eutectic when there is a liquid formed whose composition can be expressed in positive amounts of the coexisting solids.

At the point at which $X^L = X^{AB}$, the equation reduces to

$$\frac{dP}{dT} = \frac{(S^{AB} - S^L)}{(V^{AB} - V^L)}$$

which is the equation of the curve giving the change of melting temperature of AB with pressure. It is also a point on the three-phase curve G + L + AB, so the melting point curve of AB is tangent to the three-phase curve at this point, which is called the minimum melting point of AB. It is the lowest temperature at which AB can exist in equilibrium with a liquid of its own composition. If $(V^{AB} - V^L)$ is negative, the minimum melting point is between the point of maximum temperature and the eutectic; if this difference is positive, it is between the point of maximum pressure and the point of maximum temperature.

From the eutectic E_2 proceed four P-T curves of univariant equilibria:

(G) $AB + B = L$

(L) $AB = G + B$

(B) $AB = L + G$

(AB) $B + G = L$

The first of these, the change in eutectic temperature with pressure, is not shown in figure 9. It is the projection of a curve within the solid model along which pressure, temperature, and composition change, and it goes indefinitely to higher temperatures and pressures unless terminated by a quadruple point at which a new phase appears. The second of these is the dissociation pressure curve of the compound AB, which goes from the invariant point to lower temperatures and pressures, and terminates at absolute zero if no new phase appears. The third of these is the solubility or three-phase curve of AB, which has just been discussed, and the fourth is the solubility of three-phase curve of B, which terminates at the triple point of B. At the triple point of B, the P-T curve of the reaction G + B = L becomes tangent to the melting point curve of B, L_B + B. The relations are entirely similar to those on the three-phase curve G + L + AB where it becomes tangent to the melting point curve of AB. If B melts with decrease in volume, the point of tangency is at a temperature below the triple point, but if B melts with increase in volume the melting point is raised by pressure and the three-phase curve has a point of maximum temperature. This part of the curve is difficult to realize when components differ greatly in volatility. Indeed, with most systems containing water and a high-melting silicate the initial part of the realizable P-T curve appears to be concave upward.

Figure 9a is a diagrammatic representation of the case that analcite melts congruently and forms a eutectic with jadeite. If analcite melts congruently, and at the eutectic the phases are G + L + A + Ne + Ab, as was shown in figure 6, the P-T curves will be similar up to the invariant point, but beyond that point the system will cease to be binary. When melting takes place incongruently, with formation of either nepheline plus albite, or of jadeite, the P-T curves are initially similar, but the quadruple point, which now is not a eutectic, lies on the three-phase curve G + L + AB at a point poorer in com-

ponent B than the composition of the compound, usually poorer than at the point of maximum pressure.

The preceding discussion in which the formation of both liquid and jadeite was assumed dealt with the case that the liquid was in the triangle H_2O—J—Ab. If the liquid had been chosen in the triangle H_2O—Ne—J, an entirely similar P-T diagram would have been obtained, with the curve (Ne) replacing (Ab) and Ne replacing Ab in the divariant fields.

Another type of quintuple point is that at which there is no liquid. If the phases are assumed to be G, A, Ne, J, and Ab, the P-T curves proceeding from it will be:

(G) $\quad Ne + Ab = A + J$
(A) $\quad Ne + Ab = G + J$
(Ne) $\quad A + Ab = G + J$
(J) $\quad A = G + Ne + Ab$
(Ab) $\quad A + Ne = G + J$

Since G, A, and J are on a straight line, (Ne) and (Ab) will coincide stable to stable; because Ne, J, and Ab are on a straight line, (G) and (A) will coincide stable to metastable. The sequence of P-T curves and divariant fields are shown in figure 10.[2] In reaction (G), analcite is an indifferent phase and does not take part in the reaction, in (A), gas is an indifferent phase, in (Ne), Ab is an indifferent phase, and in (Ab), Ne is an indifferent phase.

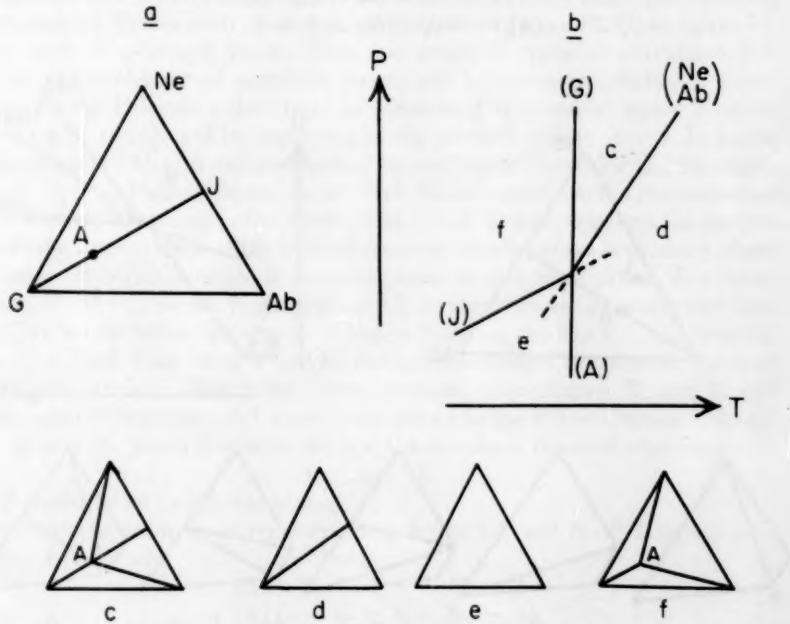

Fig. 10. The sequence of P-T curves around the quintuple point gas-analcite-nepheline-jadeite-albite.

[2] Essentially the same diagram is given by Yoder (1950).

Reaction (J), or A = G + Ne + Ab, represents the dissociation of analcite with formation of gas, crystalline nepheline, and albite. At temperatures and pressures below that line any mixture of these components is in the region in figure 10e, and the only stable phases are gas, nepheline, and albite. If a mixture in this region is compressed, on reaching the curve (J), analcite should form, and the reaction should continue until either all the water is consumed, giving the region A + Ne + Ab (fig. 10f); or until all the nepheline is consumed, giving the region G + A + Ab, or until all the albite is consumed, giving the region G + A + Ne. This curve would proceed in the one direction to absolute zero, in the other until jadeite is formed at the assumed invariant point G + A + Ne + J + Ab. It may be, however, that this invariant point is metastable with respect to the invariant point G + L + A + J + Ab (fig. 7 or fig. 8) or the similar invariant point G + L + A + Ne +J. In other words, liquid may be formed before the pressure gets great enough for the formation of jadeite.

At another type of quintuple point, gas is absent and the phases are L, A, Ne, J, and Ab. From it proceed the following P-T curves:

(L)	(A) + Ne + Ab = J
(A)	Ne + Ab = L + J
(Ne)	A + J = L + Ab
(J)	A + Ne = L + Ab
(Ab)	A + Ne = L + J

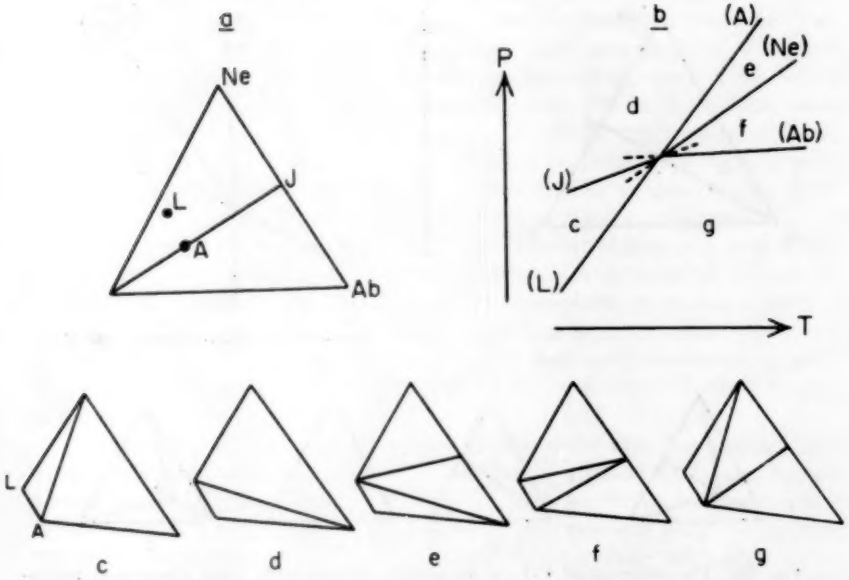

Fig. 11. The sequence of P-T curves around the quintuple point liquid-analcite-nepheline-jadeite-albite.

In figure 11, the assumed composition of the liquid gives rise to a quadrilateral L-Ne-Ab-A; other assumptions would change the set of reactions and the sequence of P-T curves and divariant regions. Since Ne, J, and Ab are on a straight line, in reaction (L), analcite is an indifferent phase, and the P-T curves (L) and (A) coincide stable to metastable. If L moved to the line ANe, (J) and (Ab) would coincide metastably; if liquid moved to AAb, (Ne) and (J) would coincide metastably, hence the metastable prolongation of (J) must lie between the stable parts of (Ne) and (Ab), as shown.

The possible phases being considered in the ternary system H_2O—Ne—Ab are six in all, namely, G, L, A, Ne, J, and Ab. Since any five of these will give an invariant point, there are six possible quintuple points in this system, namely:

Q_1	G + L + A + Ne + J
Q_2	G + L + A + Ne + Ab
Q_3	G + L + A + J + Ab
Q_4	G + L + Ne + J + Ab
Q_5	G + A + Ne + J + Ab
Q_6	L + A + Ne + J + Ab

Some of these will be stable quintuple points, others will be metastable, and only experiment can decide which is which. Of these, Q_2 has been discussed in figures 2-6, allowing the liquid to take all possible positions. Q_3 was discussed in figures 7 and 8, and the changes to be made in figures 7 and 8 for the phase assemblage of Q_1 has been discussed. Q_5 is shown in figure 10, Q_6 in figure 11. From these 6 quintuple points there can arise 15 types of univariant P-T curves, and each pair of quintuple points will be connected, stably or metastably, by the P-T curve they have in common. For example, figure 7 represents Q_3; Q_1 and Q_3 will be connected by the curve G + L + A + J. In figure 7 this curve is (Ab); if the analogue of figure 7 were drawn for Q_1, this curve G + L + A + J would be the curve (Ne). These curves are the projection on the P-T plane of curves in the hyperprism P-T-X-Y, and represent the projection of the intersections of the hypersurface on which jadeite is primary phase with that on which analcite is primary phase in that hyperprism. The curve G + L + A + J in the projection of this hyperprism on its triangular base (fig. 7a) would follow the course of liquid L across the line GA and into the triangle G-Ne-J. This curve would be the boundary curve between the fields of jadeite and analcite. Along this curve pressure, temperature, X, and Y will change, and if this entire P-T curve were drawn in the P-T projection it would join Q_1 and Q_3. When L was on the line GA the phase reaction would be

$$A = G + L$$

and J would be an indifferent phase.

Quintuple point Q_5 is represented in figure 10, and the P-T curves proceeding from it are

(Ab)	G + A + Ne + J
(J)	G + A + Ne + Ab
(Ne)	G + A + J + Ab
(A)	G + Ne + J + Ab
(G)	A + Ne + J + Ab

Q_5 will be connected either stably or metastably with Q, by the P-T curve (Ab); with Q_2, by (J); with Q_3, by (Ne); with Q_4, by (A); and with Q_6 by (G). Curve (J) in figure 10 is the curve G + A + Ne + Ab, but in figure 2 the same equilibrium is represented by the curve (L); in both cases it goes from the quintuple point to lower temperature and will terminate at absolute zero. But Q_5 may be metastable with respect to Q_2, and the reaction may be terminated at Q_2 by the formation of liquid. Similarly Q_5 and Q_3 are connected in figure 10 by the curve (Ne) or G + A + J + Ab and in figure 7 by the same equilibrium now represented by (L). (L) in figure 7 is terminated by formation of liquid, and is the extension to higher temperatures of the curve (Ne) in figure 10. Every P-T curve must either go from absolute zero to a quintuple point or join two quintuple points, and in general the decision must depend on experiment. It also is possible that two curves in a P-T projection may cross, but refer to equilibria in different regions of the composition range, and thus do not intersect in fact. The considerations in the preceding discussion determine the sequence of P-T curves around an invariant point, but they do not determine the actual position of the P-T curves, and they do not discriminate between stable and metastable quintuple points.

In the preceding some of the possible phase-equilibrium relations in the system water—nepheline—albite have been considered by deducing the sequence of the P-T curves around five of the six possible quintuple points in the system. It is assumed that the only phases to be considered are gas, liquid, analcite, nepheline, jadeite, and albite. The possible formation of hydronepheline, natrolite, or quartz has been excluded, as well as formation of solid solution. The distribution of the divariant fields around each quadruple point has been deduced, and the correlation between the P-T curves and the boundary curves in the usual triangular phase equilibrium has been indicated.

It has been assumed that the composition of the gas phase is pure water, or so nearly pure water as not to affect the shape of the various composition triangles or to produce the additional solid phase to be expected if the equilibria were not ternary but quaternary. Also, the entire subject of critical phases and critical end points has been ignored. It only assumes importance when the P-T-X-Y hypersurface joining the critical points of the three components is intersected by the saturation hypersurface of a compound, and most of the phase-equilibrium studies are not in this region.

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THE CRYSTALLINE MODIFICATIONS OF $NaAlSi_3O_8$

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ABSTRACT. X-ray studies of synthetic albites reveal a wide variation in lattice parameters of the crystals, depending on the conditions of crystallization.

A glass of composition $NaAlSi_3O_8$ has been crystallized in the presence of water vapor under pressure, at temperatures between 450°C and 1000°C for varying periods of time. X-ray study of the crystals reveals that at each temperature the crystals formed after a few hours are similar to high-temperature albite in lattice parameters. Experiments of longer duration, however, show that the lattice parameters of the initially formed crystals change gradually and finally reach a steady value which is characteristic of the temperature of crystallization. The results suggest that for each temperature there is a stable crystalline form of $NaAlSi_3O_8$ which is intermediate between high-temperature albite and low-temperature albite, high-temperature albite being stable only above about 1000°C and low-temperature albite only below about 450°C.

Previous investigations have indicated that some natural potassium feldspars may have crystallized metastably as the high-temperature monoclinic modification, sanidine, and subsequently inverted to the low-temperature triclinic modification, microcline. The experiments reported here support a similar conclusion in the case of sodium feldspar, namely that some natural albites now in the low-temperature form may have crystallized metastably in the high-temperature form and gradually inverted to the low-temperature form. The variations in the properties of albites from low-temperature veins of Alpine type are consistent with this interpretation.

INTRODUCTION

The purpose of this paper is to present the results obtained from a study of the crystalline forms of $NaAlSi_3O_8$ (albite) in the system $NaAlSi_3O_8$—H_2O and to describe the synthesis of crystals corresponding fairly closely to the low-temperature form of albite.

The first experimental work which indicated that there was more than one crystalline modification of $NaAlSi_3O_8$ was due to Merwin (1911), who observed under the microscope changes in the double refraction of alkali feldspars during and after heating in a high-temperature microscope stage. He suggested that albite had two forms; the transition temperature of the low-temperature (β) form to the high-temperature (α) form he gave as about 900°C. Between 1911 and 1950 a number of studies were made of the effect of heating natural albites from pegmatites; among these were the works of Barth (1931) and Spencer (1937). Measurements of the optical properties of natural sodium-rich feldspars from volcanic rocks had led a number of investigators to believe that chemical composition was not the only factor which determined the optical properties, and in 1941 Köhler proposed that there were two series of plagioclases, a high-temperature and a low-temperature series. Oftedahl (1948) suggested that there might be a continuous transition from the high- to the low-temperature series.

In 1950 Tuttle and Bowen showed that there were two distinct modifications of $NaAlSi_3O_8$, which they described as high-temperature albite and low-temperature albite.[1] They found that albite synthesized in the laboratory had X-ray and optical properties different from those of natural albites from pegmatites but that the natural albites could, in some cases, be converted to a form essentially the same as the synthetic material by prolonged heating at a temperature near the melting point. The synthetic crystals were all of the high-temperature form even when crystallized at temperatures as low as 250°C.

[1] These terms are sometimes abbreviated to high-albite and low-albite.

A monoclinic form of $NaAlSi_3O_8$ was reported by Barbier and Proust (1908) and to this form Schaller (1911) gave the name "barbierite." It was, however, subsequently discredited. In 1952 the present writer found that some of the high-temperature albites synthesized in the laboratory acquired monoclinic symmetry at elevated temperatures but reinverted to triclinic symmetry even on rapid cooling.[2] In the course of this study (MacKenzie, 1952) slight differences were found between the albites synthesized in the laboratory, depending on the temperatures at which they were crystallized; these differences were (a) slight variations in the spacings of certain critical reflections in the X-ray diffraction patterns and (b) variations in the temperature at which the symmetry became monoclinic, the crystallization temperature being inversely related to the temperature of inversion to monoclinic symmetry. Slight differences in the X-ray diffraction patterns of sodium-rich plagioclases synthesized in the laboratory at varying temperatures had been noted previously by Tuttle and Bowen (personal communication from Dr. Bowen, 1951), but the patterns were in all cases similar to that of the high-temperature form and no investigation was made of the differences.

The more detailed study of the rock-forming minerals had led to an increasing awareness of the possible importance of small differences in the physical properties of the minerals. Although slight differences in optical and other properties of different samples of a mineral are usually attributed to substitution of other atoms, in many cases it is possible that the physical conditions at the time of crystallization may be partly responsible for the variations. The present study was aimed at determining more about the differences which had been detected in synthetic albites and at the same time learning something about the nature of the change from the high-temperature to the low-temperature form, and, if possible, synthesizing the low-temperature form.

EXPERIMENTAL METHODS

The starting material for the synthesis of albite was in every case a homogeneous glass of composition $NaAlSi_3O_8$. A glass prepared by J. W. Greig was employed (Greig and Barth, 1938), when all this was used J. F. Schairer kindly prepared a new batch of glass, and thereafter D. B. Stewart kindly supplied a batch of glass prepared by him. No differences of any kind could be detected in the three glasses or in the albite crystallized from them under identical conditions.

It is extremely difficult to crystallize albite glass (Day and Allen, 1905; Bowen, 1913). Greig and Barth (1938) prepared crystalline albite free from all but small traces of glass by growing the crystals under a small pressure of water vapor in sealed silica glass tubes. Schairer and Bowen (1956) have recently discussed how it is possible to obtain a small amount of crystals, without the aid of water pressure, if the glass is previously annealed at successively lower temperatures for long periods of time. Bowen and Tuttle (1950) found

[2] Since this monoclinic form cannot be quenched and observed at room temperature there seems to be no reason to give it a special mineralogical name, and it is referred to here as monoclinic $NaAlSi_3O_8$.

that under a water vapor pressure of 15,000 p.s.i. a glass of albite composition could be completely crystallized in from 30 minutes to an hour.

The crystallization of albite in the present study was accomplished in all cases in the presence of water vapor under pressure, using Tuttle cold-seal pressure vessels (Tuttle, 1949). For each experiment a sample of $NaAlSi_3O_8$ glass, ground so that the largest particles were less than 0.05 mm in size and weighing about 40 mg, was contained in a small platinum tube along with about 10 mg of distilled water. The platinum capsules, 3/4 inch in length and 3/32 inch inside diameter, were cleaned in warm HCl, washed with distilled water and annealed before being used. For each experiment the capsule was first weighed, distilled water introduced with a small pipette and the capsule reweighed. The glass was next introduced, and the capsule was closed by squeezing the end with a small pair of pliers and weighed again. The end of the capsule was then welded and the capsule was reweighed. The object of welding the capsule is to make it gas tight to ensure a closed system. After every run the capsules were weighed and a gain or loss in weight indicated that the capsule had leaked. All runs in which the capsules leaked were discarded. As many as four capsules could be contained in the pressure vessel at one time, but at temperatures above about 700°C the capsules tend to stick together, so no more than three were inserted in one bomb. The required pressure was applied by pumping water into the pressure vessel, and the deformation of the walls of the platinum capsule ensures that the water pressure inside the capsule is equal to the applied pressure outside. The pressure of the water supplied by the pump was measured by a Bourdon gauge, and the values given are believed to be accurate to better than $\pm$ 5 percent of the measured value. The temperature was measured by chromel-alumel thermoelements and continuously recorded on a Brown recording potentiometer. Temperatures were controlled by Brown temperature regulators and in short runs of up to 48 hours are believed to be accurate to $\pm$ 5°C and in longer runs to $\pm$ 10°C.

The products of each run were examined under the petrographic microscope to determine whether or not the material was completely crystalline. In almost every run it was found that a small amount of glass remained, but for all practical purposes the charge could be considered as completely crystalline. In one or two cases the runs were discarded when, for one reason or another, the amount of glass present was appreciable. Because of the small size of the crystals it was impossible to make any optical measurement on them. X-ray powder diffraction patterns were made of the crystalline product of each experiment.

The most suitable method of distinguishing between high- and low-temperature albite is to measure the difference in 2θ values of the 131 and $1\bar{3}1$ reflections in an X-ray powder diffraction pattern (Tuttle and Bowen, 1950).[3] For low-temperature albite the value of $2\theta_{131}—2\theta_{1\bar{3}1}$ was given by Tuttle and Bowen as 1.06° and for high-temperature albite 2.03° for filtered copper radiation. It has been found that this angular difference is very sensitive to the conditions under which the albite has been crystallized and so it has been

[3] Smith (1956) has pointed out that the 131 reflection was wrongly indexed as $\bar{1}32$ by Tuttle and Bowen.

measured for the crystalline products of each run and the values are tabulated along with the other data for the runs.

The value of $2\theta_{131}$—$2\theta_{1\bar{3}1}$ is used here to indicate the relationship of a particular synthetic albite to high-temperature albite on the one hand and low-temperature albite on the other hand. Because this study is based to a large extent on the variations in $2\theta_{131}$—$2\theta_{1\bar{3}1}$, it is convenient to limit the use of the terms high-temperature albite and low-temperature albite to those materials in which $2\theta_{131}$—$2\theta_{1\bar{3}1}$ is greater than 2.00° and less than 1.15°, respectively. All other specimens will be described as intermediate albites. It would be desirable to measure more than one parameter for this purpose, but this would involve many long calculations from careful measurements of the X-ray diffraction patterns, whereas the measurement of $2\theta_{131}$—$2\theta_{1\bar{3}1}$ is readily carried out. The X-ray powder diffraction patterns were made using a Norelco high-angle X-ray diffractometer. The required range in 2θ (32.5°-29.5° for CuKα) was scanned at least six times at 0.25° per minute and the chart speed set to record 1° of 2θ per inch. The settings used were: scale factor 1, multiplier 1 and time constant 16. The slits on the goniometer were as follows: divergent slit 1°, receiving slit 0.006 inch and scatter slit 1°. Large sharp peaks were obtained for the 131 and $1\bar{3}1$ reflections by using the low value for the scale factor. The absolute positions of the reflections were not determined but merely the differences, and these were measured from the centers of the peaks at a third of the distance from the top, using a ruler designed specially for this purpose. The mean value of the six or more measurements was taken in each case. The patterns were measured to 0.005 inch, and on the same pair of peaks the measurements were reproducible to better than ± 0.010 inch. However, on different pairs of peaks from the same chart, variations of as much as 0.04 inch were found in one or two cases.[4] Dr. F. Chayes very kindly calculated that the error attached to the mean values of $2\theta_{131}$—$2\theta_{1\bar{3}1}$ quoted here is 0.004 inch in 95 percent of the measurements.

The values of $2\theta_{131}$—$2\theta_{1\bar{3}1}$ have been measured from X-ray diffraction patterns recorded at room temperature, and it is known that the value of $2\theta_{131}$—$2\theta_{1\bar{3}1}$ is sensitive to the temperature of the specimen when the X-ray diffraction pattern is made (MacKenzie, 1952). The error introduced into the measurements by variations in room temperature is so small that it can be neglected in the present work. It must be borne in mind, however, that the values of $2\theta_{131}$—$2\theta_{1\bar{3}1}$ quoted throughout this paper are for specimens X-rayed at room temperature and very different values would be obtained if in each case the specimen was X-rayed at the temperature of synthesis.

RESULTS

Preliminary Remarks

The first series of experiments was made to determine the magnitude of the variation in the value of $2\theta_{131}$—$2\theta_{1\bar{3}1}$ in albite with temperature of crystal-

[4] When the goniometer is set to "oscillate" the required range in 2θ is scanned from high angle to low angle and then from low angle to high angle: It has been found in some cases that those parts of the pattern in which the scanning is in the direction of decreasing 2θ give a mean value of $2\theta_{131}$—$2\theta_{1\bar{3}1}$, differing from those in which the scanning is in the direction of increasing 2θ. In every case the average value of all measurements has been taken.

lization as reported by MacKenzie (1952). A glass of composition $NaAlSi_3O_8$ was crystallized at a series of temperatures from 500°C-1000°C; the water vapor pressures and the duration of the runs were not the same for each temperature and there were a number of reasons for this. At 600°C the water pressure used was 28,000 p.s.i. and the time of the run was 41 hours; under these conditions the product of the run was almost completely crystalline and gave a good X-ray diffraction pattern. At 1000°C the water pressure used was 2500 p.s.i. and the time of the run was 5 hours; a much shorter time for the higher temperature was used so as to prolong the life of the Stellite pressure vessel. The maximum water pressure which can be used in the crystallization of albite at temperatures between 825°C and 1000°C was obtained from the curve determined by Goranson (1938), showing the projection of the three-phase curve albite + liquid + vapor on the temperature-pressure plane in the system $NaAlSi_3O_8$—H_2O.

It was found very early in this study that the duration of the experiments was very important in determining the nature of the crystals as well as the temperature of crystallization. It is possible that the water pressure might affect the results also, and so in all subsequent series of experiments the conditions were such that only one of the three variables temperature, water vapor pressure and time was changed, while the other two were fixed. A fourth variable is the size of the crystals formed, but this is related to the size of the particles of glass used and may be related to the crystallization temperature and the duration of the experiment. This will be discussed in a following section, but for the present it is sufficient to state that, in all cases where we are considering the variables temperature, time and water pressure, the grain size of the glass was kept as nearly uniform as possible, since this is the chief factor which determines the size of the crystals formed. The smaller the crystals are the more readily will equilibrium between the crystals and the vapor be established, and so it is desirable that the crystals be small.

Relation between Temperature of Crystallization and $2\theta_{131}$—$2\theta_{1\bar{3}1}$

Glass of composition $NaAlSi_3O_8$ was crystallized at a series of temperatures from 400°C to 875°C under a water vapor pressure of 14,000 p.s.i., the duration of each experiment being 24 hours. For each temperature at least two runs were made, and the values of $2\theta_{131}$—$2\theta_{1\bar{3}1}$ obtained from the products of each run are given in table 1. Where the numbers of the runs made at any one temperature are consecutive the experiments were made at the same time in the same bomb; where the numbers are not consecutive they were made independently of each other at different times. Figure 1 shows a plot of the values of $2\theta_{131}$—$2\theta_{1\bar{3}1}$ against temperature for the temperature range 400°C-875°C, and to draw attention to the nature of the relation a smooth curve has been drawn through the points. This curve has been extended by a broken line to 1000°C through points marked with crosses at 900°C and 1000°C; at these temperatures the water vapor pressure used was less than 14,000 p.s.i. and so the results should not be compared directly with those at lower temperatures. It is believed, however, that any error introduced by comparing the results of the

TABLE 1

Values of $2\theta_{131}$—$2\theta_{1\bar{3}1}$ for Albites Crystallized at Different Temperatures (P_{H_2O} = 14,000 p.s.i.; time = 24 hours)

Run	Temp.(°C)	$2\theta_{131}$—$2\theta_{1\bar{3}1}$	Run	Temp.(°C)	$2\theta_{131}$—$2\theta_{1\bar{3}1}$
302	400	1.926	80	650	1.915
303	400	1.933	89	650	1.933
			130	650	1.933
352	425	1.900			
353	425	1.908	79	675	1.940
354	425	1.920	90	675	1.931
355	425	1.935			
			85	700	1.940
291	450	1.922	86	700	1.948
292	450	1.912			
			77	725	1.939
289	475	1.904	91	725	1.938
290	475	1.904			
			81	750	1.950
269	500	1.878	82	750	1.946
270	500	1.866	178	750	1.944
286	500	1.888	179	750	1.952
275	525	1.822	277	775	1.933
276	525	1.838	278	775	1.930
281	525	1.836			
			74	800	1.945
287	550	1.833	127	800	1.954
288	550	1.835			
			73	825	1.948
273	575	1.871	279	825	1.947
274	575	1.877	280	825	1.950
283	575	1.866			
284	575	1.866	1	850	1.955
			116	850	1.949
83	600	1.915	117	850	1.960
84	600	1.909			
			2	875	1.973
271	625	1.926	126	875	1.971
272	625	1.924			

experiments at 900°C and 1000°C with those made at higher water vapor pressure is slight and can be neglected at the present time.

It can be seen that there is no simple relation between temperature of crystallization and the value of $2\theta_{131}$—$2\theta_{1\bar{3}1}$ for runs of 24 hours' duration. For temperatures greater than 550°C there is a tendency for increased temperature of crystallization to result in an increased value of $2\theta_{131}$—$2\theta_{1\bar{3}1}$, although in the range 700°C-850°C there is very little variation with temperature. At some temperature in the range 525°C-550°C a reversal of the general relation suggested occurs and the value of $2\theta_{131}$—$2\theta_{1\bar{3}1}$ increases with decrease in temperature of crystallization. This was an unexpected result and no completely satisfactory explanation can be proposed for this; the following observations may, however, be relevant, but a fuller discussion of this question is left to a later section of this paper.

The reversal of the effect of temperature on the value of $2\theta_{131}$—$2\theta_{1\bar{3}1}$ was not noted until this study was well advanced, since the preliminary experiments were not made at temperatures below 500°C and were at 100° intervals of

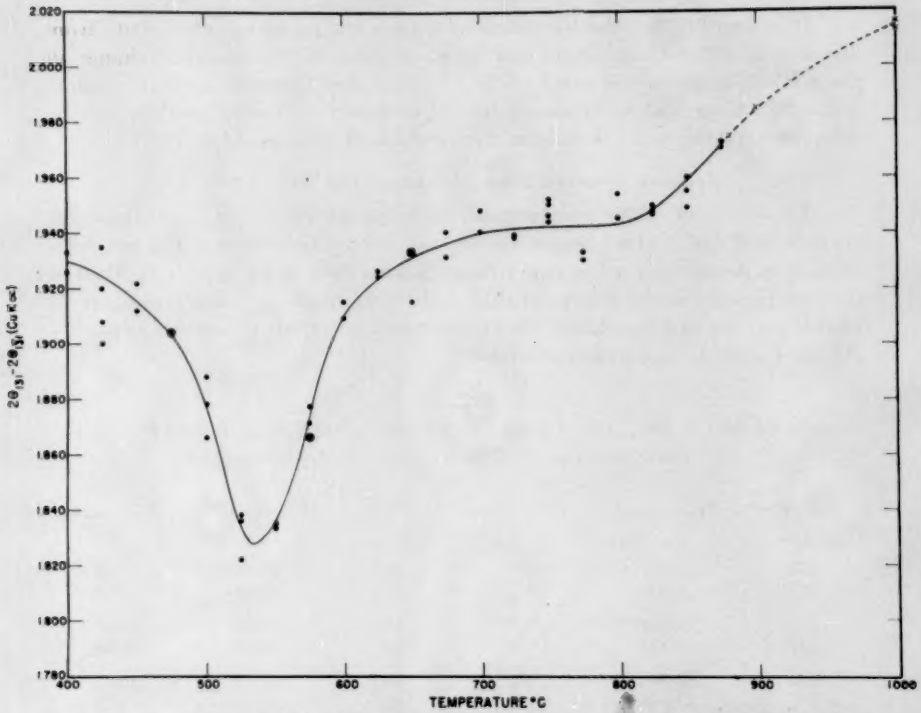

Fig. 1. Values of $2\theta_{131}—2\theta_{\bar{1}3\bar{1}}$ of synthetic albites plotted against crystallization temperature. In the temperature range 400°C to 875°C the experiments were of 24 hours' duration at a water vapor pressure of 14,000 p.s.i. The crosses at 900°C and 1000°C represent the results of experiments made at lower water vapor pressures and are therefore not strictly comparable with the results of experiments made at $P_{H_2O} = 14{,}000$ p.s.i.

temperature. It was noted subsequently, however, that at 400°C the value of $2\theta_{131}—2\theta_{\bar{1}3\bar{1}}$ was greater than that obtained at 500°C in an experiment of the same duration. Examination of the complete X-ray diffraction pattern of the crystals prepared at 400°C revealed two lines, in addition to those of albite; these two lines corresponded with the two most intense reflections in the X-ray diffraction pattern of analcite. In two runs made at 300°C and a water vapor pressure of 28,000 p.s.i. for 1390 hours the only phase which could be detected optically or by X-rays was analcite. Either this analcite contains excess silica over that required by the formula $NaAlSi_2O_6 \cdot H_2O$ or possibly the excess SiO_2 is present in a form which does not produce good reflections in the X-ray diffraction pattern.[5]

[5] It seems remarkable that from a glass of albite composition only analcite crystallizes. It might be suspected that the total composition of the solid material of these charges, which apparently consist of analcite only, differs considerably from the original glass of composition $NaAlSi_3O_8$. One of these charges (apparently consisting of analcite only) was held at 950°C in the presence of water vapor at 14,000 p.s.i., and under these conditions a hydrous glass is formed. The temperature was lowered to 700°C and held for one hour. Examination of the resulting product under the petrographic microscope revealed only albite crystals; if the bulk composition of the material had been $NaAlSi_2O_6 \cdot H_2O$, crystallization at 700°C under a water pressure of 14,000 p.s.i. would have produced albite + nepheline and the nepheline could be very easily detected under the microscope (MacKenzie, unpublished data on the system $NaAlSiO_4$—$NaAlSi_3O_8$—H_2O).

It is possible that the formation of even a small amount of analcite from the glass of albite composition may be responsible for the observed change in the relation between the value of $2\theta_{131}$—$2\theta_{1\bar{3}1}$ and temperature in the range below 525°C or 550°C. It should be noted, however, that no analcite can be detected optically or by X-rays in the products of runs made at 500°C.

Relation between Water Pressure and $2\theta_{131}$—$2\theta_{1\bar{3}1}$

The effect of water pressure on the value of $2\theta_{131}$—$2\theta_{1\bar{3}1}$ obtained for crystals held for a given length of time at a fixed temperature has not been studied in detail, only a few experiments having been made at 700°C. Most of the experiments in the course of this study were made at a water pressure of 14,000 p.s.i. or just less than 1000 atmospheres, since this pressure was readily obtained with the equipment available.

TABLE 2

Values of $2\theta_{131}$—$2\theta_{1\bar{3}1}$ for Albites Crystallized at Different Water Pressures (Temperature = 700°C; time = 16 hours)

Run	P_{H_2O}(p.s.i.)	$2\theta_{131}$—$2\theta_{1\bar{3}1}$	Run	P_{H_2O}(p.s.i.)	$2\theta_{131}$—$2\theta_{1\bar{3}1}$
133	7,000	1.950	128	35,000	1.951
134	7,000	1.957	129	35,000	1.951
131	14,000	1.956	136*	59,000	1.940
132	14,000	1.953	137*	59,000	1.940
124	28,000	1.962	110*	88,000	1.867
125	28,000	1.962	111*	88,000	1.871

* Runs made by H. S. Yoder, Jr.

A series of runs was made at 700°C at water pressures from 7000 p.s.i. to 88,000 p.s.i., the duration of each run being 16 hours. Dr. H. S. Yoder kindly agreed to make the runs at 59,000 p.s.i. and 88,000 p.s.i. The results of these runs are given in table 2 and the values of $2\theta_{131}$—$2\theta_{1\bar{3}1}$ are plotted against pressure in figure 2. For this series of experiments it appears that between 7000 p.s.i. and 35,000 p.s.i. the water pressure has no significant effect on the value of $2\theta_{131}$—$2\theta_{1\bar{3}1}$ obtained but that above this pressure the value of $2\theta_{131}$—$2\theta_{1\bar{3}1}$ falls rapidly with increased water pressure.

At 525°C a number of runs of duration up to 400 hours were made at both 14,000 p.s.i. and 28,000 p.s.i. water pressure, and no difference could be detected between the results of the runs made at the two different pressures.

Since it is known that water pressure is necessary for promoting the changes in the lattice parameters with time, it is likely that at higher water pressures the crystals will reach the equilibrium form for a particular temperature more rapidly than at lower water pressures. Despite this advantage of using a high water pressure most of the experiments reported here were made at 14,000 p.s.i. since the range of temperatures which could be used would have been very limited if pressures of the order of 70,000 p.s.i. were used. The role of water pressure in promoting the changes in lattice parameters of albite will be discussed in a subsequent section.

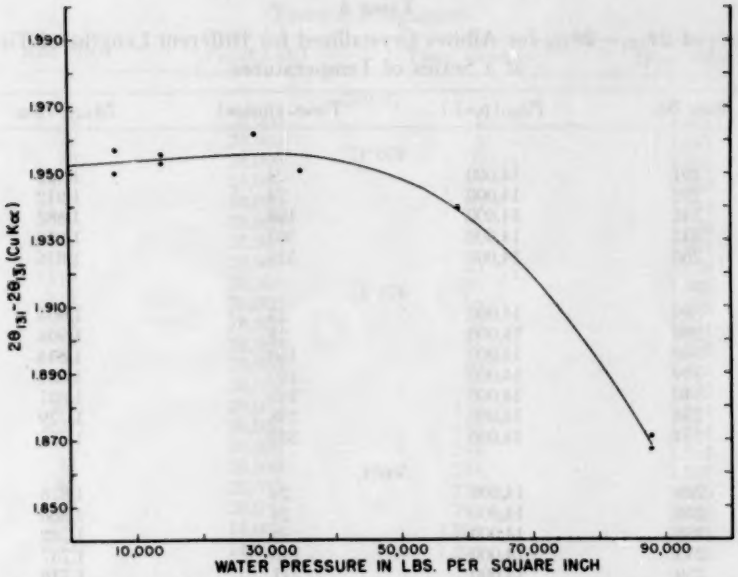

Fig. 2. Values of $2\theta_{131}$—$2\theta_{\bar{1}31}$ of synthetic albites plotted against water vapor pressure in a series of experiments made at constant temperature (700°C) and for a constant time (16 hours).

Relation between Time of Crystallization and $2\theta_{131}$—$2\theta_{\bar{1}31}$

Undoubtedly the most important observation which has resulted from this study is that the lattice parameters of the crystalline material depend to a large extent on the duration of the experiment. At a temperature of 700°C and a water pressure of 14,000 p.s.i. albite glass is nearly all crystalline after 30 minutes; the present study shows that if the run is kept at temperature and pressure for say four days the lattice constants of the crystals change continuously, presumably by reaction with the hydrous vapor, so that the crystalline material obtained from an experiment of 4 days' duration has a different value of $2\theta_{131}$—$2\theta_{\bar{1}31}$ from that obtained after 30 minutes.

A series of experiments of durations varying from 1 hour to 3000 hours have been made at the following temperatures: 1000°C, 900°C, 850°C, 800°C, 750°C, 700°C, 600°C, 525°C, 500°C, 475°C and 450°C. Runs at 1000°C were made at a water pressure of 2000 p.s.i., those at 900°C and a few of those at 525°C were made at 7000 p.s.i. and those at 700°C were made at 28,000 p.s.i. The remaining runs were made at 14,000 p.s.i. The results of these runs are set down in table 3. Because of the long time required for many of the experiments it was not convenient to have only one charge in a pressure vessel for periods of a month or more. In most cases at the beginning of the run four charges were inserted in the pressure vessel. After a given time at a certain pressure and temperature, the pressure vessel was quenched, the pressure released and the charges removed and weighed. Provided that none of the capsules had leaked, three of them were replaced in the pressure vessel, the

TABLE 3

Values of $2\theta_{131}$—$2\theta_{\bar{1}31}$ for Albites Crystallized for Different Lengths of Time at a Series of Temperatures

Run No.	P_{H_2O} (p.s.i.)	Time (hours)	$2\theta_{131}$—$2\theta_{\bar{1}31}$
		450°C	
291	14,000	24	1.922
292	14,000	24	1.912
341	14,000	168	1.882
342	14,000	307	1.846
263	14,000	525	1.816
		475°C	
289	14,000	24	1.904
290	14,000	24	1.904
348	14,000	150	1.844
349	14,000	150	1.834
340	14,000	168	1.827
253	14,000	238	1.779
254	14,000	503	1.725
		500°C	
269	14,000	24	1.878
270	14,000	24	1.866
258	14,000	96	1.782
245	14,000	148	1.737
259	14,000	211	1.718
246	14,000	428	1.633
268	14,000	531	1.586
247	14,000	620	1.559
218	14,000	1,220	1.489
248	14,000	1,579	1.493
252	14,000	2,178	1.461
219	14,000	2,680	1.410
		525°C	
275	14,000	24	1.822
276	14,000	24	1.838
281	14,000	24	1.836
325	7,000	44	1.824
326	7,000	44	1.815
321	7,000	71	1.788
293	14,000	192	1.730
318	7,000	474	1.663
320	7,000	474	1.669
295	14,000	888	1.594
		600°C	
83	14,000	24	1.915
84	14,000	24	1.909
234	14,000	45	1.867
235	14,000	45	1.868
186	14,000	52	1.859
215	14,000	120	1.844
188	14,000	151-1/2	1.832
189	14,000	151-1/2	1.840
200	14,000	262	1.819
201	14,000	262	1.824
190	14,000	359	1.805
191	14,000	359	1.805
233	14,000	835	1.766
221	14,000	926	1.752
220	14,000	1,761	1.730

TABLE 3 (Continued)

Run No.	P_{H_2O}(p.s.i.)	Time (hours)	$2\theta_{131}-2\theta_{121}$
		700°C	
26	28,000	1	1.964
27	28,000	3	1.961
30	28,000	5-1/2	1.955
135	28,000	12	1.959
18	28,000	20	1.934
19	28,000	20	1.936
20	28,000	20	1.931
22	28,000	20	1.926
112	28,000	50	1.903
113	28,000	50	1.896
28	28,000	74	1.891
29	28,000	74	1.890
98	28,000	90	1.885
99	28,000	90	1.892
108	28,000	138	1.864
109	28,000	138	1.864
31	28,000	234	1.864
33	28,000	234	1.862
62	28,000	278	1.850
70	28,000	791	1.806
229	14,000	1,200	1.793
230	14,000	1,200	1.799
		750°C	
81	14,000	24	1.950
82	14,000	24	1.946
178	14,000	24	1.944
179	14,000	24	1.952
180	14,000	53	1.926
181	14,000	53	1.924
182	14,000	144	1.895
183	14,000	144	1.901
194	14,000	238	1.899
195	14,000	238	1.889
184	14,000	248	1.887
185	14,000	248	1.893
192	14,000	384	1.890
193	14,000	384	1.888
223	14,000	1,085	1.884
222	14,000	1,422	1.883
		800°C	
74	14,000	24	1.945
127	14,000	24	1.954
56	14,000	32	1.949
170	14,000	50	1.920
171	14,000	50	1.920
145	14,000	70	1.933
146	14,000	70	1.930
57	14,000	78-1/2	1.921
216	14,000	92	1.930
172	14,000	139	1.912
173	14,000	139	1.922
198	14,000	262	1.929
199	14,000	262	1.927
196	14,000	384	1.921
197	14,000	384	1.914
224	14,000	1,103	1.928
225	14,000	1,440	1.925

TABLE 3 (Continued)

Run No.	P_{H_2O}(p.s.i.)	Time (hours)	$2\theta_{131}-2\theta_{1\bar{3}1}$
	850°C		
174	14,000	7	1.971
175	14,000	7	1.981
1	14,000	24	1.955
116	14,000	24	1.949
117	14,000	24	1.960
42	14,000	50	1.943
161	14,000	97	1.943
169	14,000	143	1.942
160	14,000	193	1.944
143	14,000	360	1.945
144	14,000	360	1.951
226	14,000	984	1.953
227	14,000	1,440	1.944
	900°C		
327	7,000	2	2.000
328	7,000	2	1.993
316	7,000	24	1.977
317	7,000	24	1.985
329	7,000	41	1.982
330	7,000	41	1.982
	1,000°C		
204	2,000	17	2.013
205	2,000	17	2.016
306	2,000	66	2.018
307	2,000	66	2.008

pressure and temperature raised to the same values as before and the experiment continued; the fourth capsule was opened and an X-ray diffraction pattern made of the charge. After a further period of time a second capsule was removed and so on until the final capsule was removed.

In one case (run 252) a different procedure was adopted, using albite already crystallized for 1220 hours at 500°C (run 218) as the starting material for a further run of 958 hours at the same temperature, instead of using albite glass. From this single experiment it is not possible to decide whether this procedure will give the same results as are obtained when the tube is not opened between successive parts of the runs. Perhaps the only way of comparing the two procedures would be to determine the value of $2\theta_{131}-2\theta_{1\bar{3}1}$ for the crystals obtained from runs of the same total duration.

The results of these experiments are plotted in figures 3 and 4. Figure 3 covers only runs up to 500 hours in duration and includes all the temperatures at which experiments were made. Figure 4 is on a much smaller scale, and most of the runs of short duration have been omitted to avoid confusing the diagram: runs at 475°C, 525°C, and 450°C are not plotted in figure 4, since all of them are of less than 525 hours' duration and they appear in figure 3.

Considering only figure 4 it appears that for each crystallization temperature there is a characteristic value of $2\theta_{131}-2\theta_{1\bar{3}1}$ which is attained fairly rapidly for temperatures above 700°C but for lower temperature the characteristic value may not be reached even after many weeks. It is not certain that these characteristic values represent equilibrium values for the particular

temperatures but experiments have been made to try to establish that these are indeed equilibrium values; these experiments will be described in a subsequent section. It appears also from figure 4 that for a given time of crystallization there is a simple relation between the value of $2\theta_{131}$—$2\theta_{1\bar{3}1}$ and the temperature of crystallization. However, when we consider figure 3, where the results

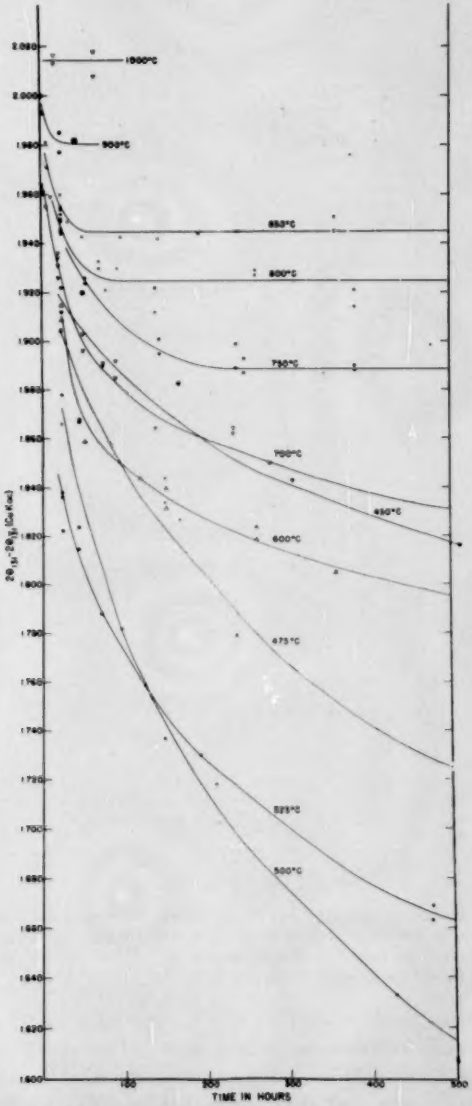

Fig. 3. Diagram showing the change in $2\theta_{131}$—$2\theta_{1\bar{3}1}$ of synthetic albites with time of crystallization for a series of temperatures from 1000°C to 450°C. Only the results of experiments of less than 525 hours' duration are plotted.

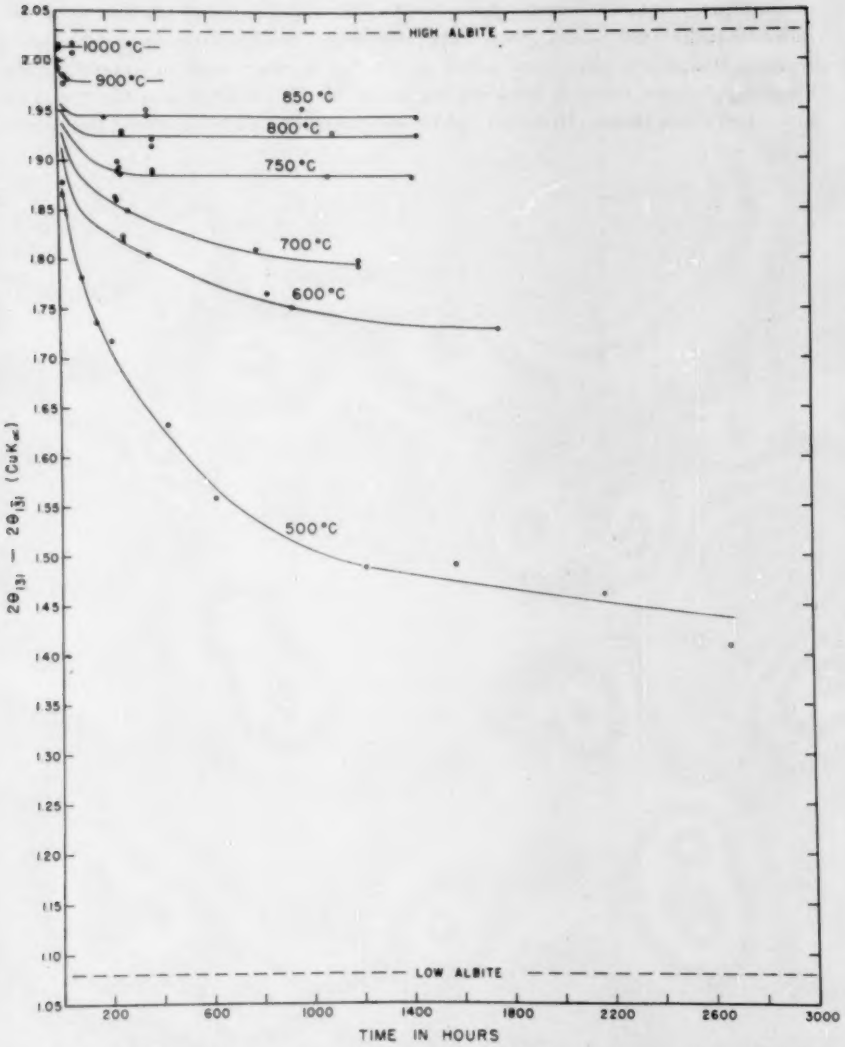

Fig. 4. The change in $2\theta_{131}-2\theta_{\bar{1}31}$ of synthetic albites with time of crystallization. Most of the results of experiments of less than 200 hours' duration have been omitted since these are plotted in figure 3. Experiments at 525°C, 475°C and 450°C have also been omitted since these are plotted in figure 3.

of a number of runs made at 450°C, 475°C, and 525° C are plotted, it can be seen that this simple relation no longer holds. The curve for 525°C crosses that for 500°C at about 100 hours; the curves for 475°C and 450°C intersect the curves for 600°C and 700°C because of their differing slopes. From this it can be seen that the relations obtained for the series of experiments made for 24 hours and plotted in figure 1 do not necessarily hold for runs of much

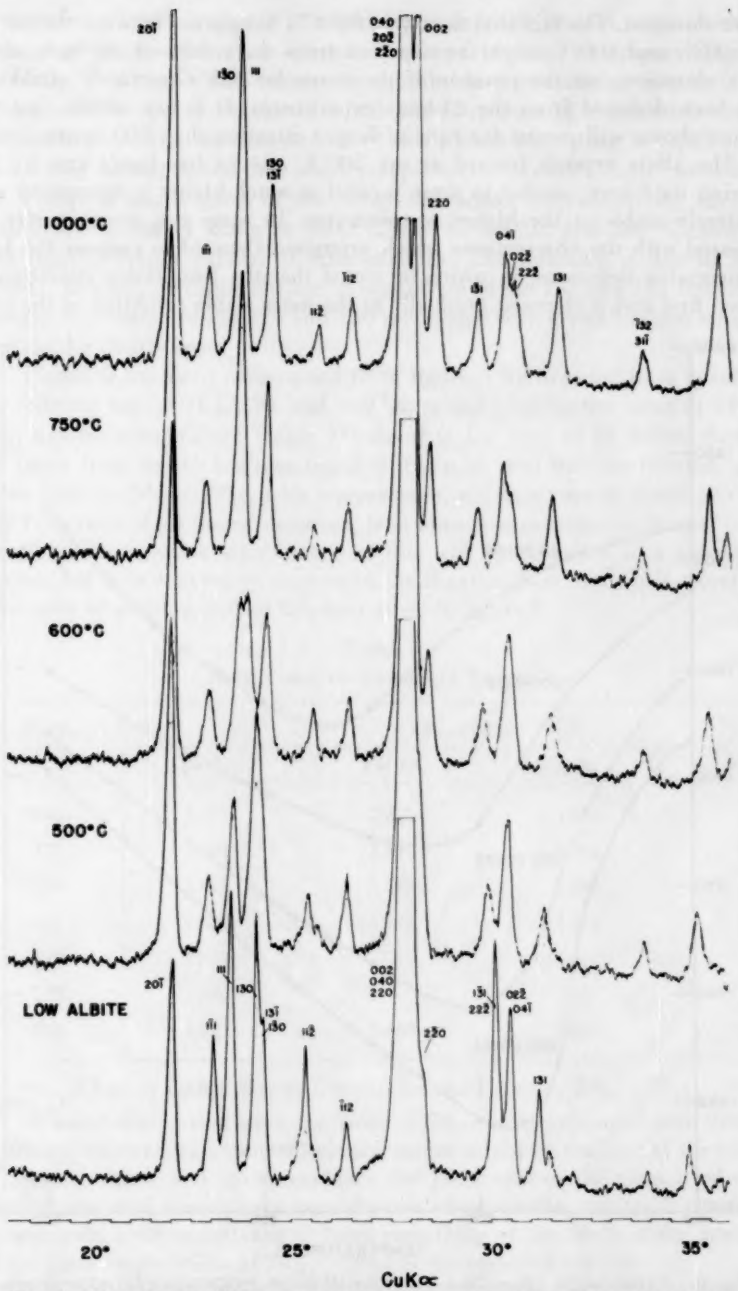

Fig. 5. X-ray powder diffraction patterns of the supposed equilibrium forms of albite at 1000°C, 750°C, 600°C and 500°C compared with that of low-temperature Amelia albite.

longer duration. The fact that the curve for 475°C appears between the curves for 500°C and 600°C might be expected from the results of the runs of 24 hours' duration, but the position of the curve for 525°C certainly could not have been deduced from the 24-hour experiments. It is not certain that the relation shown will persist for runs of longer duration than 500 hours.

The albite crystals formed at say 500°C after a few hours are, by the criterion used here, similar to those formed at much higher temperatures and apparently stable at the higher temperatures. In some respects this may be compared with the observations which prompted Ostwald to propose the Law of Successive Reactions, in which he stated that the least stable condition is formed first and is changed gradually to the more stable condition at the tem-

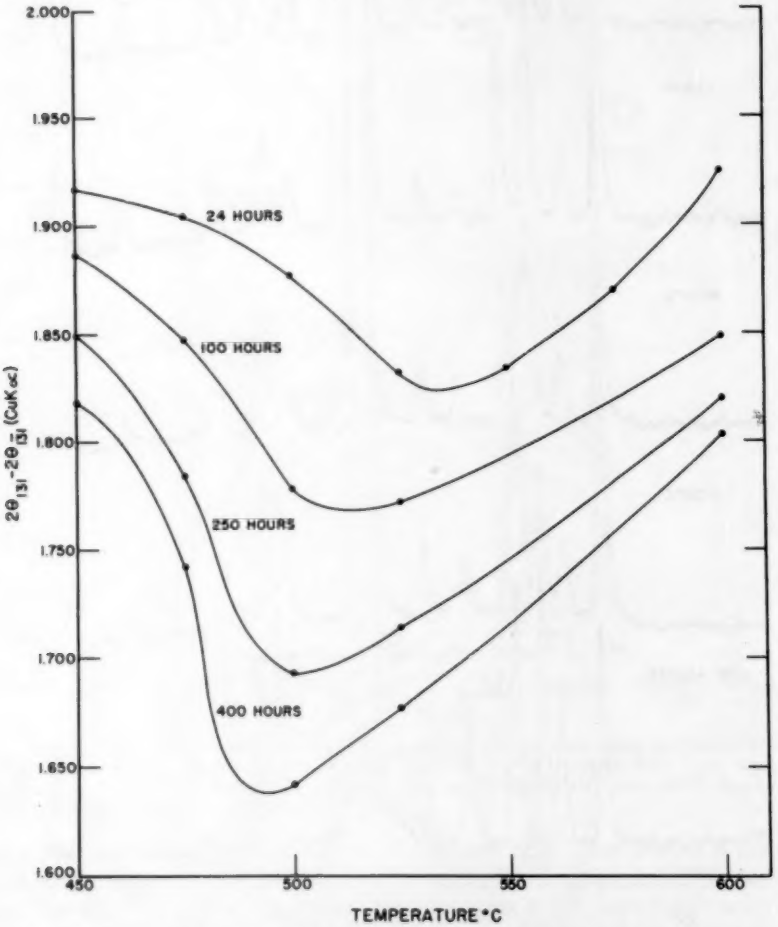

Fig. 6. Variations in $2\theta_{131}$—$2\theta_{\bar{1}31}$ with crystallization temperature for experiments of 24, 100, 250 and 400 hours' duration. The data used to construct this diagram are given in table 4.

perature considered. It should be noted, however, that Ostwald was considering phase changes in which there is a temperature or a range of temperatures over which the two phases can coexist in equilibrium; whereas we are here concerned with a type of change in which the properties of the crystals change continuously, and at no time are there two phases coexisting in equilibrium. Also it may be mentioned that many exceptions to Ostwald's "Law" are known.

Figure 5 shows parts of the X-ray diffraction patterns of the supposed equilibrium forms of albite at 1000°C, 750°C, 600°C, and 500°C compared with the diffraction pattern of Amelia albite. The indexing is due to Smith (1956). In addition to the change in separation of the 131 and $1\bar{3}1$ reflections, changes in position of the 220 and 130 reflections with crystallization temperature can be clearly seen.

Figure 6 has been constructed from figure 3 by drawing lines parallel to the ordinate axis at 100, 250, and 400 hours and plotting the value of $2\theta_{131}$—$2\theta_{1\bar{3}1}$ against temperature (table 4); the data for runs of 24 hours' duration are taken from figure 1. From figure 6 it can be seen that the reversal of the curve relating $2\theta_{131}$—$2\theta_{1\bar{3}1}$ with temperature, which occurs at about 525°C to 550°C in runs of 24 hours' duration, is at lower temperature in runs of longer duration. The possible significance of this will be discussed in a subsequent section, but it is convenient to present the diagram here since it is merely another way of plotting part of the data given in figure 3.

TABLE 4

Data Used to Construct Figure 6

Temp. (°C)	$2\theta_{131}$—$2\theta_{1\bar{3}1}$			
	24 hr.	100 hr.	250 hr.	400 hr.
450	1.917	1.886	1.849	1.818
475	1.904	1.847	1.784	1.742
500	1.877	1.778	1.693	1.642
525	1.832	1.772	1.714	1.677
550	1.834	—	—	—
575	1.870	—	—	—
600	1.912	1.849	1.820	1.803

Effect of Grain Size of Crystals on the Value of $2\theta_{131}$—$2\theta_{1\bar{3}1}$

It was believed that since the value of $2\theta_{131}$—$2\theta_{1\bar{3}1}$ changed with duration of the experiment an important consideration might be the size of the crystals of albite formed, and in consequence the grain size of the glass used as the starting material would have considerable effect on the results. A number of experiments were undertaken to learn something of the effect of the grain size of the glass on the value of $2\theta_{131}$—$2\theta_{1\bar{3}1}$ of the resulting crystals.

Glass which had had only a preliminary crushing was seived to give three fractions: one between 60 and 150 mesh, one between 150 and 200 mesh and

a third less than 200 mesh. Microscopic examination of the third fraction revealed that a large number of grains were about 0.1 mm in their largest dimension. About 150 mg of this material was ground by hand in a new agate mortar for about 30 minutes, and as a result the average grain size was reduced to about 0.02 mm in size. These four samples of glass were used as starting materials for runs at 425°C and P_{H_2O} = 14,000 p.s.i. for 24 hours in the same pressure vessel. The values of $2\theta_{131}$—$2\theta_{1\bar{3}1}$ were measured from the X-ray diffraction patterns of the products of these runs and are set down in table 5. In figure 1 the four points plotted for 425°C are the results of these runs. The figures suggest that the value of $2\theta_{131}$—$2\theta_{1\bar{3}1}$ is indeed affected by the grain size of the glass and that the smaller the fragment of glass the smaller will be the value of $2\theta_{131}$—$2\theta_{1\bar{3}1}$.

TABLE 5

Effect of Grain Size of Glass on $2\theta_{131}$—$2\theta_{1\bar{3}1}$ of Crystals

Run No.	Size of glass particles	$2\theta_{131}$—$2\theta_{1\bar{3}1}$
352	~0.02 mm.	1.900
353	<200 mesh (~0.1 mm.)	1.908
354	150-200 mesh	1.920
355	60-150 mesh	1.935

In a number of other experiments two runs inserted in the same pressure vessel under the same conditions revealed that the smaller the grain size of the glass the lower the value of $2\theta_{131}$—$2\theta_{1\bar{3}1}$ obtained. Since the grain size of the glass was not carefully controlled the results of these runs are not tabulated.

Microscopic examination of the crystals prepared in runs 352-355 showed that the crystals were largest when the large fragments of glass were used. In the case of the most finely ground glass the crystals were of the order of 1 micron in size. It was noticeable that the reflections on the X-ray diffraction pattern were considerably sharper and more intense in the case of the larger crystals. The amount of glass which had not crystallized appeared to be greater in the case of the charge with the largest fragments of glass, but it is very difficult to compare the proportion of glass to crystals in charges of different grain size, since the uncrystallized fragments of glass remaining are large when the grain size of the initial glass is large.

If one assumes that crystallization of a glass in the presence of water vapor commences at the surface of the glass grains it is to be expected that the crystals growing from the smaller grains of glass will be smaller than those growing from larger grains of glass. In addition, if it is assumed that the changes which occur in the crystals with time take place from the surfaces of the crystals inwards, then it is to be expected that the smaller crystals will change more rapidly with time than will the larger crystals.

One experiment was carried out to try to substantiate the belief that the change in the crystalline material begins at the surface of the crystals and

works inwards. It has been found that one method of growing large crystals of albite is to use as the starting material fairly large pieces of glass in which some water is already dissolved. A charge of finely ground albite glass together with about 10 mg of water was held at 920°C and 30,000 p.s.i. for 1 hour to saturate the glass with water. The charge was quenched and on examination no crystals were seen. It was then crushed just enough so that the pieces of glass could be inserted in a fresh platinum capsule and 10 mg of water added. This charge was held at 500°C and 14,000 p.s.i. for 531 hours and with it in the same pressure vessel was a charge of finely ground anhydrous albite glass plus water. After the completion of the run the values of $2\theta_{131}$—$2\theta_{1\bar{3}1}$ were measured for both materials. The control run using finely ground glass gave a value for $2\theta_{131}$—$2\theta_{1\bar{3}1}$ of 1.586° (run 268, table 3), and the run using the hydrated glass gave 1.815°. Examination of the product of the latter run revealed crystals of albite up to 0.1 mm in length, and in some of the crystal fragments the extinction of the edges differed from that of the cores, giving the appearance of zoned plagioclase crystals. The X-ray diffraction pattern, however, showed no sign of the presence of two phases, but showed well-defined peaks representing 131 and $1\bar{3}1$ reflections from one phase. If the rims of the crystals have different lattice parameters from the cores, as the extinction would suggest, it may be that these differences are too slight to be resolved in the powder diffraction patterns. In a following section, devoted to the hydrothermal treatment of low-temperature albite, the question of the coexistence of two phases of albite composition but of differing lattice parameters will be discussed more fully.

In the light of the foregoing discussion the shape of the curves in figures 3 and 4 must be considered as applicable only to the grain size of glass used here. If great care was taken to grind the glass very much more finely it might be that the curves would appear very different. However, it is believed that the steady values of $2\theta_{131}$—$2\theta_{1\bar{3}1}$ for each temperature do represent equilibrium values and so would not be affected by the grain size of the glass or the crystals formed from it. If the grain size of the crystals was very much smaller the equilibrium values would be reached more quickly.

Much of the uncertainty of the positions of the points in figures 1, 3 and 4 may be attributed to differences in the grain size of the starting material rather than to uncertainties in the measurement of temperature, water pressure or $2\theta_{131}$—$2\theta_{1\bar{3}1}$.

INTERPRETATION OF RESULTS

Introduction

Before discussing the interpretation of the results of the experiments described in the previous section it is necessary to clarify a number of the problems which arise from these results. The next few pages will be devoted to a discussion of the problems of interpretation of the results and to a description of a number of experiments designed to solve some of these problems.

In any phase equilibrium studies it is of the utmost importance that the composition of the phases be known as accurately as possible. If a carefully prepared glass of given composition can be crystallized to a single crystalline

phase with only the slightest trace of glass remaining, then the composition of the crystalline material is known fairly accurately. However, when water is used as a flux some uncertainty arises because it is known that water vapor under pressure may leach preferentially certain constituents from a glass.[6] It was for this reason that all the experiments described here were carried out in sealed platinum capsules.

Since most silicate minerals are only sparingly soluble in water, it would in most cases be reasonable to neglect the change in composition of crystals in contact with vapor in a sealed capsule and to assume that the single crystalline phase had the same composition as the original glass. In the present study, however, we are concerned with very small changes in the crystal lattice which might be interpreted as resulting from slight variations in composition of the crystals from that of the original glass. It may be argued that the composition of the crystals is changed gradually with time until the vapor comes to equilibrium with the crystals and that the variation in composition of the crystals is reflected in the decrease in $2\theta_{131}$—$2\theta_{1\bar{3}1}$ with increasing time until equilibrium is established. It is to be expected, however, that a close approach to chemical equilibrium between the crystals and vapor will be established in minutes or at the most in a few hours even at 500°C so that this explanation of the observed variation in $2\theta_{131}$—$2\theta_{1\bar{3}1}$ is most unlikely.[7] It would be desirable to be able to demonstrate that the crystals formed in all the runs have exactly the composition $NaAlSi_3O_8$ and a few experiments have been designed to try to establish that this is indeed the case. An attempt has been made to show that the characteristic values of $2\theta_{131}$—$2\theta_{1\bar{3}1}$ for each temperature are equilibrium values for the specimens quenched to room temperature. A more precise definition of the equilibrum value of $2\theta_{131}$—$2\theta_{1\bar{3}1}$ would necessitate that this be determined at the temperature of the experiment by X-raying the sample at high temperature. This has not been done in the present work.

Effect of Dry Heating Intermediate Albites at 1080°C

From the work of Tuttle and Bowen (1950) it is known that some low-temperature albites can by heating at a temperature not far below the melting point be converted to the high-temperature form. It was considered that, if the intermediate albites synthesized were heated at 1080°C in the dry way so that the value of $2\theta_{131}$—$2\theta_{1\bar{3}1}$ changed to that characteristic of high-temperature albite, this would be some evidence that the crystals were indeed of composition $NaAlSi_3O_8$. Dr. Schairer kindly agreed to carry out the heating of four samples of synthetic albites; these were heated for 7 days at 1080°C and X-ray patterns made. The same samples were then heated for a further period of 14 days at 1080°C. The results of the measurements of $2\theta_{131}$—$2\theta_{1\bar{3}1}$ on these

[6] A glass of composition $Ab_{99.2}Qtz_{99.8}$ contained in an open capsule was held at 700°C at a water vapor pressure of 30,000 p.s.i. for 260 hours. Examination of the charge revealed nepheline crystals near the open end of the capsule, some nepheline and albite lower down and albite crystals with a small amount of glass at the bottom. Since the bulk composition of the original charge was richer in SiO_2 than albite, a considerable amount of SiO_2 must have been removed from the capsule in the vapor.

[7] Since the different crystalline forms will have slightly different solubilities in water vapor, strictly speaking equilibrium between crystals and vapor will not be reached until the equilibrium form of the crystals at a particular temperature is obtained.

TABLE 6

Effect on $2\theta_{131}—2\theta_{1\bar{3}1}$ of Heating Synthetic Albites at 1080°C for 7 Days and 21 Days

Original Run No.	Temp. of crystallization (°C)	Time of crystallization (hours)	$2\theta_{131}—2\theta_{1\bar{3}1}$		
			Before heating	Heated 7 days	Heated 21 days
144	850	360	1.951	1.988	2.008
196	800	384	1.921	1.964	1.985
192	750	384	1.890	1.963	1.962
190	600	359	1.805	1.911	1.925

samples before and after each period of heating are given in table 6. Unfortunately, these results are inconclusive since only the sample initially crystallized at 850°C reached a value of $2\theta_{131}—2\theta_{1\bar{3}1}$ close to that of high-temperature albite. The remaining specimens changed in the expected direction, but it is probable that the duration of heating was not long enough to achieve the final value for high-temperature albite.

Tuttle and Bowen (1950) found that certain low-temperature albites were much more readily converted to the high-temperature form than others, but could give no explanation for this observation. It is possible that some factor in the crystallization history is responsible for the differing response of low-temperature albites to heat treatment at 1080°C. It was anticipated that the synthetic albites would reach the high-temperature form much more rapidly than a low-temperature natural mineral, but clearly this is not the case, and no satisfactory explanation for this can be presented at this time.

Hydrothermal Treatment of Amelia Albite

As a result of a number of experiments on heating Amelia albite in the presence of sodium disilicate solution in water under pressure, Tuttle and Bowen (1950) came to the conclusion that the high-temperature albite—low-temperature albite inversion may be near 700°C. They state that "At 775° Amelia albite changed to the high modification in 3 days, and at 720° the change took place in 2 weeks, whereas at 675° no evidence of change was found on heating for three weeks." Tuttle and Bowen, however, go on to say that "there is no assurance that longer heating at lower temperatures will not cause transformation, and a definite value for the inversion temperature cannot be regarded as established."

The results of the experiments reported in this study cannot be reconciled with the idea of a fixed inversion temperature for the high-low inversion, but indicate that there are an infinite number of intermediate forms between the low-temperature form and the high-temperature form. It would appear most unlikely, therefore, that a natural low-temperature albite, if held at say 800°C in the presence of water vapor under pressure, could ever change so that the value of $2\theta_{131}—2\theta_{1\bar{3}1}$ reached the maximum value which we have considered to be that of high-temperature albite.

To determine more about the change which takes place when Amelia albite is heated in the presence of water vapor under pressure, two charges of an analyzed sample of finely ground Amelia albite were held at 800°C at P_{H_2O} = 14,000 p.s.i. in sealed platinum capsules. One charge was removed after 90 hours and the second charge after 311 hours; both charges were X-rayed and the values of $2\theta_{131}$—$2\theta_{1\bar{3}1}$ measured. These values are given in table 7. In the X-ray diffraction pattern made from the run of 90 hours' duration there were four reflections which were interpreted as 131 and $1\bar{3}1$ of two feldspar phases. The value of $2\theta_{131}$—$2\theta_{1\bar{3}1}$ measured from one pair of reflections corresponded to a feldspar close to low-temperature albite and that from the other pair to a feldspar intermediate between high-temperature albite and

TABLE 7

Hydrothermal Treatment of Amelia Albite at 800°C

Run No.	P_{H_2O}(p.s.i.)	Time (hours)	$2\theta_{131}$—$2\theta_{1\bar{3}1}$
298	14,000	90	(a) 1.210 (b) 1.848
297	14,000	311	1.844

low-temperature albite. The X-ray pattern of the run of 311 hours' duration showed a single pair of reflections corresponding to 131 and $1\bar{3}1$ of one feldspar phase, and the difference in 2θ values of these reflections was almost the same as that of the intermediate phase in the run of 90 hours' duration.

Microscopic examination of the product of the run of 90 hours' duration revealed that the crystal fragments had retained their angular shape and the rims of many of the fragments had different extinction angles from the cores. In their experiments on heating Amelia albite in the dry way Tuttle and Bowen (1950) found a similar feature when they examined partly inverted material under the microscope and they concluded that the inversion begins at the surfaces of the grains and gradually migrates inwards.

In the hydrothermal experiments the coexistence of two phases, one near low-temperature albite and the other an intermediate temperature phase, is shown to be a disequilibrium state by the disappearance of the low-temperature phase in the longer experiment, the final product being a single phase intermediate between high- and low-temperature albite.

It is important to notice that the value of $2\theta_{131}$—$2\theta_{1\bar{3}1}$ obtained for the single phase (1.844) is considerably less than that characteristic of high-temperature albite. It is, however, lower than the supposed equilibrium value for 800°C (1.925). This may be accounted for by the specimen not being pure albite; its composition by chemical analysis is $Or_{1.4}Ab_{98.2}An_{0.4}$ (Emmons, 1953), and it is known that the effect of both potassium and calcium is to lower the value of $2\theta_{131}$—$2\theta_{1\bar{3}1}$ from that of pure albite. Some confirmation of this is given by dry heating experiments on samples of the same analyzed specimen of Amelia albite carried out by J. R. Smith. Smith found that heating this sample for 2 weeks at 1080°C produced a value for $2\theta_{131}$—$2\theta_{1\bar{3}1}$ of

1.970 and heating for an additional period of three weeks produced no further change (J. R. Smith, personal communication). The expected value for $2\theta_{131}$—$2\theta_{1\bar{3}1}$ of pure albite in the high-temperature form is 2.03.

These experiments do not establish that the steady value of $2\theta_{131}$—$2\theta_{1\bar{3}1}$ for 800°C is an equilibrium value, but the results are in harmony with this conclusion. If the value of $2\theta_{131}$—$2\theta_{1\bar{3}1}$ obtained after treating Amelia albite hydrothermally at 800°C had been near that of high-temperature albite, then the data in figures 3 and 4 would require a very different interpretation from that which has been given above.

In a previous section we discussed the optical appearance of large crystals synthesized at 500°C in which the extinction on the edges of the grains differed from that in the cores and noted that the X-ray diffraction pattern showed no sign of the presence of two feldspar phases. In that case the possible difference between $2\theta_{131}$—$2\theta_{1\bar{3}1}$ of the two phases was very slight and so did not even cause noticeable broadening of the peaks in the diffraction pattern. In the present case, however, the difference between $2\theta_{131}$—$2\theta_{1\bar{3}1}$ of the two phases was measured to be about 0.64°, and so it is to be expected that the reflections from each phase will be resolved.

Effect of Subjecting an Intermediate Albite to a Higher or Lower Temperature than That of Initial Crystallization

It might be expected that an albite crystallized at some temperature should, if held at a higher or lower temperature in the presence of water vapor under pressure for sufficient time, eventually acquire a value of $2\theta_{131}$—$2\theta_{1\bar{3}1}$ characteristic for the new temperature. Two charges of albite glass were crystallized at 600°C, P_{H_2O} = 14,000 p.s.i., for 120 hours. Only one of the capsules was opened and the value of $2\theta_{131}$—$2\theta_{1\bar{3}1}$ determined; the other capsule was returned to the pressure vessel and held at 800°C, P_{H_2O} = 14,000 p.s.i., for a further 92 hours and the value of $2\theta_{131}$—$2\theta_{1\bar{3}1}$ determined. The results of this experiment are given in table 8. The charge which was opened after 120 hours at 600°C was used as a control run, and it was found that the value of $2\theta_{131}$—$2\theta_{1\bar{3}1}$ for this run fell close to the expected value derived from the curve showing the relation between $2\theta_{131}$—$2\theta_{1\bar{3}1}$ and time for a temperature of 600°C (fig. 3); it was assumed that the charge which was not opened would also have a value of $2\theta_{131}$—$2\theta_{1\bar{3}1}$ close to the expected value. From figure 3 it can be seen that when glass is crystallized at 800°C a steady value of $2\theta_{131}$—$2\theta_{1\bar{3}1}$ (= 1.925°) is reached after about 100 hours. The effect of holding the crystals synthesized at 600°C at a temperature of 800°C has been to raise the value of $2\theta_{131}$—$2\theta_{1\bar{3}1}$. The crystals formed at 600°C do not acquire the steady value of $2\theta_{131}$—$2\theta_{1\bar{3}1}$ for 800°C as readily as do crystals initially synthesized from glass at 800°C. The observation that the value of $2\theta_{131}$—$2\theta_{1\bar{3}1}$ increases does, however, indicate that the change is in the direction anticipated.

A similar experiment was made by crystallizing glass at 800°C for 92 hours and then holding the crystals at 600°C for 162 hours at P_{H_2O} = 14,000 p.s.i. In this case the value of $2\theta_{131}$—$2\theta_{1\bar{3}1}$ was reduced but did not reach as

TABLE 8

Effect on $2\theta_{121}$—$2\theta_{\bar{1}31}$ of Subjecting Crystals to Higher or Lower Temperature than That of Initial Crystallization

Run No.	Initial Crystallization				Subsequent Treatment of Crystals				Expected value of $2\theta_{121}$—$2\theta_{\bar{1}21}$ under the same conditions as subsequent treatment of crystals, using glass as starting material
	P_{H_2O} (p.s.i.)	Temp. (°C)	Time (hours)	$2\theta_{131}$—$2\theta_{\bar{1}31}$	P_{H_2O} (p.s.i.)	Temp. (°C)	Time (hours)	$2\theta_{131}$—$2\theta_{\bar{1}31}$	
214	14,000	600	120	—	14,000	800	92	1.897	1.925
215	14,000	600	120	1.844					
216	14,000	800	92	1.930					
217	14,000	800	92	—	14,000	600	162	1.885	1.835
93	14,000	700	791	1.843	51,000	600	832	1.806	1.742
94	51,000	600	832	1.742					

low a value of $2\theta_{131}—2\theta_{1\bar{3}1}$ as would glass crystallized at 600°C for 162 hours. The results of this experiment are given in table 8.

It has already been noted that crystals were used instead of glass as the starting material for a run of long duration since it was considered that the times of holding crystals in the presence of vapor under pressure and at elevated temperature were additive. Thus to find the value of $2\theta_{131}—2\theta_{1\bar{3}1}$ for crystals synthesized at 500°C and held for 400 hours it is possible to use crystals which were obtained from a run of 150 hours' duration and hold them for a further 250 hours under the same conditions of temperature and pressure. In the very earliest stages of this study it was thought that in order to synthesize an albite with as low a value of $2\theta_{131}—2\theta_{1\bar{3}1}$ as possible time might be saved by using crystals already prepared, and for which the value of $2\theta_{131}—2\theta_{1\bar{3}1}$ was much less than the maximum value of about 2.03°, as the starting material for further experiments. One experiment, however, showed that this assumption was quite incorrect. In table 8 the results of two runs, nos. 93 and 94, show that the value of $2\theta_{131}—2\theta_{1\bar{3}1}$ is very much less when a glass is used as the starting material in a run at 600°C and $P_{H_2O} = 51{,}000$ p.s.i. than when the starting material consists of crystals synthesized at 700°C.

These experiments show that our initial assumption that the durations of runs are additive can be valid only when successive runs on the same charge are made under the same conditions of temperature and perhaps also water vapor pressure. It seems that the temperature of initial crystallization is an important factor in determining the response of the crystals to further heat treatment. Thus two samples of synthetic albite having identical values of $2\theta_{131}—2\theta_{1\bar{3}1}$ may differ in certain physical properties because of differences in their crystallization history. The differing response of natural low-temperature albites, having initial values of $2\theta_{131}—2\theta_{1\bar{3}1}$ which are identical, to heating at 1080°C has been attributed to differences in crystallization history.

Role of Water in Promoting Changes in the Lattice Parameters of Albite

It has already been noted that Greig and Barth (1938) and Bowen and Tuttle (1950) found that the presence of water vapor under pressure greatly facilitates the crystallization of a glass of albite composition, but we must now consider what part the water vapor plays in effecting the changes which have been measured in the crystalline albite. A few experiments indicate that no changes can be produced, in the time of laboratory experiments, in either natural low-temperature albites or in synthetic albites, except at temperatures near the melting point, unless water vapor is present. Two of these experiments only will be mentioned briefly.

A charge consisting of albite crystals synthesized at 700°C and $P_{H_2O} = 14{,}000$ p.s.i. for 24 hours was enclosed in a platinum capsule but no water was added. The capsule was subjected to a pressure of 28,000 p.s.i. at 700°C and on removal after 140 hours no change in the value of $2\theta_{131}—2\theta_{1\bar{3}1}$ from that of the original crystals could be detected. Dry heating experiments on low-temperature albite at atmospheric pressure at about 700°C produced no measurable change in the value of $2\theta_{131}—2\theta_{1\bar{3}1}$.

Crystalline albite is only sparingly soluble in water vapor and it is as yet not known under what conditions, if any, the solubility is congruent. However, if the charge is at a uniform temperature, a close approximation to equilibrium between vapor and crystals will be established fairly rapidly at any given temperature. In the hydrothermal treatment of low-temperature albite the optical appearance of the crystals, which have not reached the equilibrium form, is similar to that found as a result of the dry heating of low-temperature albite, and, as Tuttle and Bowen (1950) concluded, this indicates that the change begins at the surface of the crystal and migrates inwards. Since the change in the crystalline material appears to take place in the same manner whether water vapor is present or not, it is of interest to inquire why the change proceeds so much more rapidly in the presence of water vapor under pressure.

It is unlikely that the changes in $2\theta_{131}$—$2\theta_{1\bar{3}1}$ which have been measured in albites, subjected to hydrothermal treatment, can be attributed to solution of the less stable form and precipitation of a more stable form as rims on the original crystals. If this were the case, mantling of the crystals by the stable form would protect the cores of these crystals from further change and the unstable form might persist indefinitely in this state. In addition, it is likely that some new centers of crystallization would form and crystals grow around these, but no such growths have been observed.

It is possible that, at elevated temperatures and vapor pressures, water is able to pass through the feldspar lattice. If the changes which have been observed in albite are due to a rearrangement of the Si and Al atoms then Al-O and Si-O bonds have to be broken and the energy necessary for breaking these strong bonds may be provided through the medium of the water vapor. It has been suggested by some investigators that water vapor under pressure may aid the unmixing of a homogeneous alkali feldspar to form a microperthite, in which the evidence that the original crystal boundaries are preserved is undeniable. Although rearrangement of the alkali ions may be effected without redistribution of the Al and Si ions, some such mechanism as that proposed above is necessary in order to explain the role of water vapor under pressure in facilitating unmixing within a single crystal. If water is able to pass through the lattice of a feldspar at elevated temperature and pressure some water would undoubtedly be trapped within the crystal on lowering the temperature and pressure and we have assumed throughout this study that no water is present in the albite lattice. Further researches may throw more light on the role of water in processes of the type described here.

The Nature of the Transition between High- and Low-temperature Albite

In discussing the change from low- to high-temperature albite, Tuttle and Bowen (1950) suggest that the sluggish nature of the transition is consistent with a reconstructive transformation or with some type of order-disorder change. They go on to say, "If it is order-disorder and at the same time sluggish, one can expect to find all intermediate stages, and it should be possible to synthesize albite with optical and X-ray properties exhibiting a complete gradation from the low to the high." Tuttle and Bowen were not able to synthesize low-albite and found no evidence of a gradational nature in the crystals

they synthesized; in addition they state that natural albitic feldspars are either high or low without evidence of intermediate states. They were led to the conclusion that the change from high- to low-albite involves some changes in addition to Al ⇄ Si order-disorder.

From the new data given in this paper it appears that there exist an infinite number of gradational forms between the high-temperature and the low-temperature form, and since natural sodium-rich feldspars with optical properties gradational between the high- and low-temperature forms have been found the relation between the two forms must be viewed in a new light.

Barth (1934) was the first to propose that the difference between sanidine and microcline might be due to a difference in the distribution of the Si and Al atoms in the two structures. Laves (1952) amplified this concept and considered that the relations between high-temperature albite and low-temperature albite were analogous to the relations between sanidine and microcline, and these could best be explained by the assumption that the Al-Si distribution is ordered in the low-temperature form and disordered in the high-temperature form.

Figure 7 shows the supposed equilibrium values of $2\theta_{131}$—$2\theta_{1\bar{3}1}$ for albite crystallized at different temperatures plotted against temperature. The data on which this diagram is based are taken from figure 4 and are set out in table 9. At temperatures below 750°C sufficient data are not available to fix the supposed equilibrium values of $2\theta_{131}$—$2\theta_{1\bar{3}1}$ with the same precision as has been achieved at higher temperatures and this may account for the fact that a smooth curve cannot be drawn through the points. In runs of 24 hours' duration the relation between crystallization temperature and $2\theta_{131}$—$2\theta_{1\bar{3}1}$ is not a simple one (see fig. 1) and the same may be true for the supposed equilibrium values of $2\theta_{131}$—$2\theta_{1\bar{3}1}$; thus it is possible that a discontinuity occurs in the curve near 700°C but clearly the data cannot be used to define the exact shape of the curve.

It appears to the writer that if the differences between albites crystallized at different temperatures are due to the degree of Al-Si order and an infinite number of transitional equilibrium forms exist between the high-temperature and low-temperature forms then we should not expect to find a transition temperature from a high-temperature form to a low-temperature form *unless some changes in addition to Al-Si ordering are involved, as suggested by Tuttle and Bowen (1950)*. Tuttle and Bowen were able to convert low-temperature albite to a higher temperature form above 700°C but not below this temperature in the presence of a sodium disilicate solution in water under pressure, and this may be accounted for by the shape of the curves in figure 4. The curve for 750°C flattens off after about 250 hours but that for 700°C is probably still changing in slope after more than 1000 hours. Tuttle and Bowen (1950) were well aware that longer heating at temperatures below 700°C might cause a change to a higher temperature form and so considered 700°C as providing only an upper limit to the inversion temperature.

Goldsmith and Laves (1954a, 1954b) have discussed at some length the sanidine-microcline relations, and, since these are considered to be analogous with the high-temperature albite—low-temperature albite relations, it is ap-

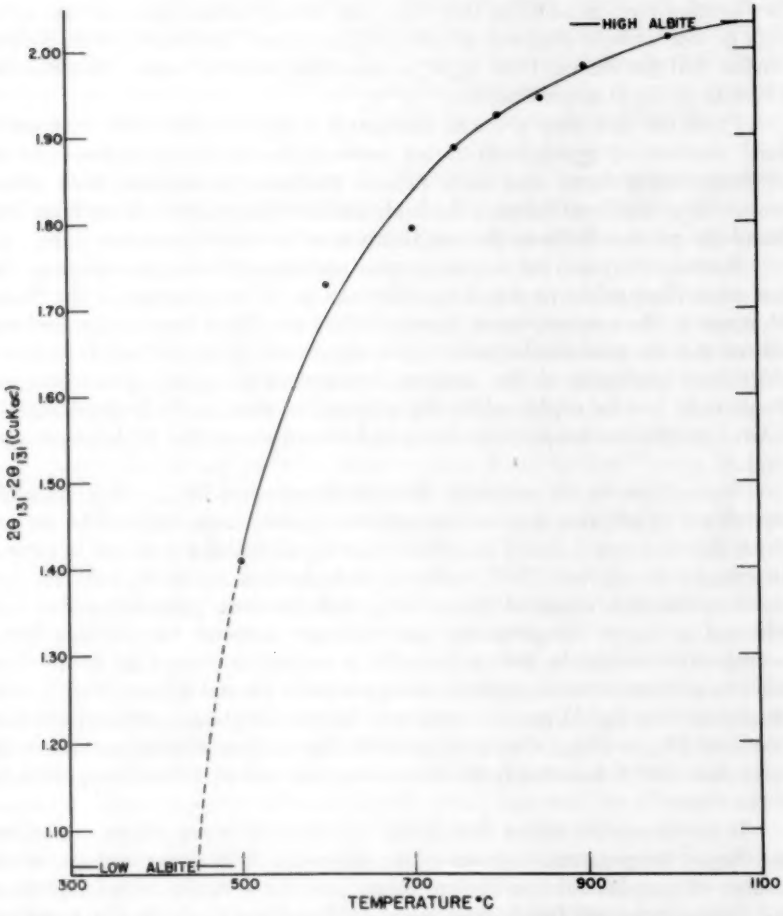

Fig. 7. Plot of the supposed equilibrium values of $2\theta_{131}-2\theta_{\bar{1}31}$ against temperature of crystallization.

propriate to look at some of their conclusions regarding the nature of the changes involved. These authors, although advocating that the difference between sanidine and microcline is due to the Al-Si distribution and that therefore there should be intermediate forms between the disordered and ordered forms, nevertheless attempt to determine an upper limit to the "inversion temperature" from microcline to sanidine. From their experiments on the hydrothermal conversion of microcline to sanidine they conclude that the "inversion temperature (T_c)" is not above approximately 500°C.

Except from the point of view of crystal symmetry, this temperature (T_c) has no particular significance if we adopt the view that there exist an infinite number of intermediate forms between a maximum microcline and a high-temperature sanidine. The fact that at some point the symmetry must change

TABLE 9
Supposed Equilibrium Values of $2\theta_{131}$—$2\theta_{1\bar{3}1}$ Taken from Figure 4

Temp. (°C)	$2\theta_{131}$—$2\theta_{1\bar{3}1}$
1,000	2.015
900	1.983
850	1.945
800	1.925
750	1.889
700	1.795
600	1.730
500	1.410

from triclinic to monoclinic does not necessitate that there is a change of phase.[8] In the case of the high-temperature—low-temperature albite relations there is, of course, no symmetry change involved at the "inversion temperature" of 700°C and so the situation is less complex.

Laves (1952) stated that there are only two stable modifications of $KAlSi_3O_8$, sanidine and microcline, and that orthoclase is not a stable form. Goldsmith and Laves (1954b) in discussing feldspars structurally intermediate between sanidine and microcline deal only with triclinic feldspars having different degrees of departure from monoclinic symmetry and apparently consider that monoclinic feldspars are structurally similar as far as the distribution of Al and Si is concerned. They explain the observed optical and X-ray differences between orthoclase and microcline as being due to the size of the units or domains making up the crystals and suggest that orthoclase may be made up of quite highly ordered domains, triclinic in symmetry, but, because of the small size of these domains, the crystals have optical and X-ray properties of monoclinic crystals.

A much more likely explanation of the variations in the properties of potassium feldspars is that these are all degrees of ordering of Al and Si from the most completely ordered maximum microcline through the intermediate microclines, orthoclases, and sanidines to the completely disordered high-sanidine. The degree of ordering of Al and Si in the monoclinic feldspars may be reflected in the variation in optical properties and in the slight changes in lattice parameters. Thus we can consider the feldspars high-sanidine, sanidine and orthoclase arbitrarily defined by optic axial angle values (Tuttle, 1952) as the monoclinic crystalline forms of $KAlSi_3O_8$ stable at certain temperatures or over certain temperature ranges as yet not known; at lower temperatures the

[8] The word phase is used here as it was defined by Gibbs. At an inversion point there is a reversible equilibrium between two phases having different thermodynamic properties and failing such a difference in properties there can be no change of phase. Gradual changes of the type with which we are concerned here are frequently described as second, or higher order, phase changes but would be more correctly described if the word phase was omitted.

intermediate microclines and maximum microcline, defined on the basis of the values of $2\theta_{131}$—$2\theta_{1\bar{3}1}$ or optic axial angle values, will each have a temperature of stable existence. The findings of Cole, Sörum and Kennard (1949) indicate that the crystallographic changes accompanying the transition from orthoclase to high-sanidine result from the disordering of Al and Si atoms.

Because of the gradational nature of the change in sodium feldspar, we might expect specimens of albite with properties intermediate between those of high-temperature albite and low-temperature albite to be of frequent occurrence just as specimens of potassium feldspars of an intermediate nature are found. With the exception of albites from pegmatites, veins and low-grade metamorphic rocks most natural sodium feldspars have significant amounts of both calcium and potassium in solid solution and these affect the value of $2\theta_{131}$—$2\theta_{1\bar{3}1}$ to some extent. We are therefore not in a position to compare the values of $2\theta_{131}$—$2\theta_{1\bar{3}1}$ of natural albites from effusive and hypabyssal rocks with those of the pure synthetic $NaAlSi_3O_8$. Optical and X-ray studies of natural sodium-rich plagioclase of known composition do, however, indicate that transitional forms do occur in the plagioclases (Oftedahl, 1948; Smith and Yoder, 1956), and Baskin (1956) has recently reported an authigenic feldspar which is virtually pure albite and is intermediate between high- and low-temperature albite in lattice parameters.

Little has been said so far regarding the non-quenchable monoclinic-triclinic symmetry change in albite (MacKenzie, 1952). It seems clear that this must involve some change other than the order-disorder change postulated for the gradation from low-temperature to high-temperature albite. When the symmetry change was first recognized little was known of the difference between albites crystallized at different temperatures, and the crystals which were used to determine the temperature of the symmetry change were not shown to be the stable forms at the crystallization temperatures. Since only crystals synthesized above approximately 950°C acquire monoclinic symmetry, it is likely that these will be close to the stable forms for the specific temperatures. No further data have been obtained on this symmetry change.

It is not improbable that potassium feldspars at high temperature exhibit a change analogous to this symmetry change in sodium feldspar. The relationship between sanidine and high-sanidine (Tuttle, 1952) may provide the parallel case, and a change of the same type as the symmetry change in sodium feldspar may be difficult to distinguish from the disordering process.

Brief mention should be made at this point of a suitable nomenclature for describing sodium feldspars. It is clearly inconvenient to use the term high-temperature albite for crystals whose properties are intermediate between those characteristic of high- and low-temperature albite. The method which has been adopted here is to define high-temperature and low-temperature albite on the basis of the values of $2\theta_{131}$—$2\theta_{1\bar{3}1}$ which can be readily measured from X-ray diffractometer patterns. Specimens having a value of $2\theta_{131}$—$2\theta_{1\bar{3}1}$ significantly different from those of high- or low-temperature albites might be conveniently described as intermediate albites; the word temperature could be omitted. Some investigators might prefer to use the value of the optic axial angle to define a sodium feldspar but at the present time only in the case of

low-temperature albite is the optic angle sufficiently accurately known (personal communication from J. R. Smith). In either case until the effects of calcium and potassium are more accurately known natural feldspars cannot be discussed in this same rigid manner we have used for synthetic albite.

PETROLOGICAL CONSIDERATIONS

The Occurrence of Low-temperature Albite in Pegmatites

The data presented in the foregoing pages indicate that a feldspar of composition $NaAlSi_3O_8$ crystallizes readily from a glass of the required composition in the presence of water vapor under pressure throughout a considerable range of temperature. It is possible that sodium feldspar with properties corresponding to those of low-temperature albite can be synthesized at 500°C given sufficient time, but the indications are that at this temperature the equilibrium form of albite is still an intermediate form and the temperature must be below 450°C for a low-temperature albite to be stable. We have noted that lowering the temperature below 500°C does not produce the desired effect of lowering the value of $2\theta_{131}$—$2\theta_{1\bar{3}1}$, at least in the water pressure range we have been considering, and so we are faced with the problem of why the albite of most pegmatites, metamorphic rocks and granites is in the low-temperature form with no evidence of intermediate temperature forms. It was tentatively suggested that the expected lowering of the value of $2\theta_{131}$—$2\theta_{1\bar{3}1}$ of albite

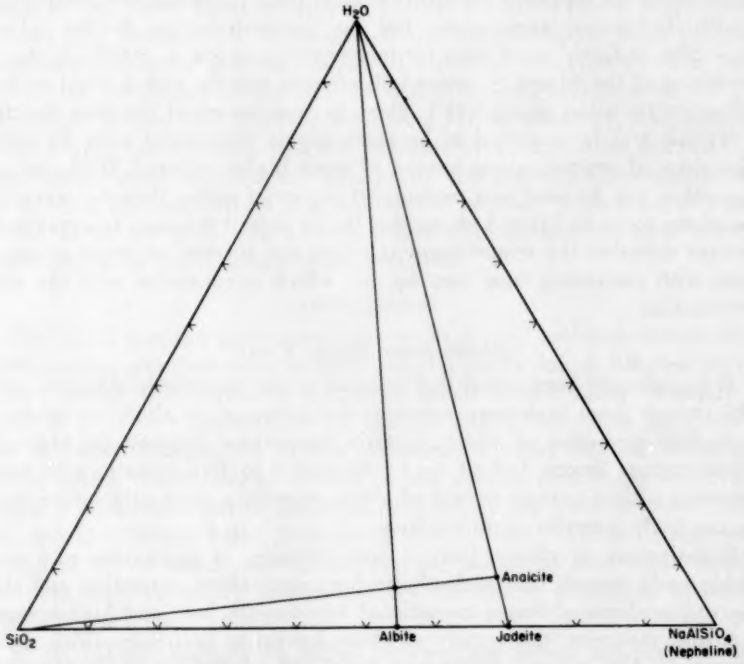

Fig. 8. Diagram showing the relations of the various phases in the system $NaAlSiO_4$—SiO_2—H_2O, plotted in weight percent.

crystallized in the laboratory was prevented by the formation of some analcite at temperatures below 500°C.

In the triangular diagram in figure 8 some of the phases in the ternary system $NaAlSiO_4$—SiO_2—H_2O are plotted. We are concerned with compositions on the join albite—water. W. S. Fyfe (personal communication) has determined the equilibrium conditions for the reaction

$$\text{analcite} + \text{quartz} \rightleftarrows \text{albite} + \text{vapor}$$

and finds that the univariant equilibrium curve for this reaction lies at about 300°C at $P_{H_2O} = 1000$ bars, i.e. about 250°C below the curve for the breakdown of analcite to albite + nepheline + vapor determined by Yoder (1954). (It is unlikely that the positions of either of these curves will be measurably affected by the form of albite produced). Thus the stable assemblage above about 300°C is albite + vapor at $P_{H_2O} = 1000$ bars and above this temperature any analcite formed metastably will eventually be replaced by albite. It is known that, in the laboratory, analcite crystallizes rapidly from a glass of suitable composition and may persist outside its stability field for a considerable time.

The failure to crystallize low-temperature albite in the laboratory, despite its common occurrence in nature, may be quite unrelated to the metastable formation of analcite and may be due to an energy barrier close to 500°C. From the shape of the curves shown in figure 4 it can be seen that the rate of attainment of the supposed equilibrium form for a particular temperature falls off with decreasing temperature, but the initial reduction in the value of $2\theta_{131}$—$2\theta_{1\bar{3}1}$ is fairly rapid even for temperatures as low as 500°C. If the rate of ordering of the Al and Si atoms falls off very rapidly with a slight decrease in temperature below about 500°C, then, in experiments of the same duration, the crystals will be expected to be more highly disordered with decreasing temperature of crystallization instead of more highly ordered. If the value of $2\theta_{131}$—$2\theta_{1\bar{3}1}$ can be used as a measure of degree of order, then the reversal in slope of the curve in figure 1 shows that this is indeed the case. In experiments of longer duration the temperature at which the reversal of slope occurs decreases with increasing time (see fig. 6), which is consistent with the above interpretation.

Albites from Alpine Veins

It has already been noted that because of the apparently sluggish nature of the change from high-temperature to low-temperature albite we might expect to find specimens of albite in states transitional between the high- and low-temperature forms. Indeed we might expect to find variations in lattice parameters within a single crystal of albite, especially since such lattice variations are fairly common in microclines.

Examination of albites from a large number of pegmatites and metamorphic rocks reveals that such albites have very sharp extinction and show no optical evidence of states transitional between the low- and high-temperature forms. However, the variety of albite known as pericline, which occurs commonly in Alpine veins, sometimes along with adularia, is characterized by very patchy extinction, and this is reflected in large variations in optic axial

angle in different parts of single crystals. The writer's attention was drawn by Dr. F. Laves to an interesting feature of these albites: the angle (σ) between the trace of the rhombic section and the *a* axis in (010) sections is frequently in the neighborhood of + 10°. The calculated value of the angle σ for low-temperature albite is + 39° 31′ (Tunell, 1952) and for high-temperature albite is – 2° 31′ (MacKenzie, 1956). It seems that the twinning was formed in a lattice, the parameters of which were not those of low-temperature albite but of some intermediate form. The variations in optical properties are consistent with the crystallization of an intermediate- or high-temperature form and incomplete conversion to the low-temperature form. The temperature of formation of the veins in which pericline and adularia occur is generally considered to be fairly low, perhaps in the region of about 300°C.

In explaining the variation in the crystallographic and optical properties of adularia Laves (1952) suggested that, if microcline is ordered with respect to Si and Al, the rate of growth of adularia may be sufficiently high that the ordering forces are overwhelmed during crystallization, producing a more or less disordered $AlSi_3O_8$ framework. Laves goes on to say that "adularia should have a tendency to change continuously to the ordered microcline state. The degree of this change would depend on the time and temperature relations and on the composition of the crystals, fluxes, etc." It is felt that, in the light of the experimental evidence obtained from the synthesis of albites, the hypothesis advanced by Laves to account for the variation in the properties of adularias may be extended to include the sodium feldspars from the same geological environment and may be stated a little more explicitly. The variability of the properties of the sodium and potassium feldspars of the type found in the Alpine veins may be accounted for by assuming that, although formed at very low temperatures, the feldspars crystallize in an intermediate- or high-temperature form but are only partly changed to the low-temperature form stable at the temperature of crystallization because, at the low water pressure and/or the low temperature of crystallization, sufficient energy to promote the ordering of Al and Si atoms is not available.

CONCLUSIONS

The belief that the differences between high- and low-temperature forms of both sodium and potassium feldspar are principally due to different degrees of order in the distribution of Al and Si atoms is now fairly generally accepted. It is to be expected that an infinite number of stable intermediate forms will exist between the highest temperature forms and the lowest temperature forms. Experimental studies in the system $NaAlSi_3O_8$—H_2O have revealed a wide variation in lattice parameters of the albite crystals synthesized, and it is believed that these variations are due to different degrees of ordering of the Al and Si atoms, although the possibility that slight chemical differences may be partly responsible for the lattice variations cannot be completely ruled out.

If an infinite number of stable intermediate forms are possible there should be no inversion temperature at which two forms may coexist in equilibrium unless some change in addition to the Al-Si order-disorder is involved,

as suggested by Tuttle and Bowen (1950). If the potassium feldspar relations are similar, the equilibrium diagram for the subsolidus region of the system $NaAlSi_3O_8$—$KAlSi_3O_8$ will show no modification lines or field boundaries except for the solvus separating the field of one feldspar from that of two feldspars.

It has already been noted that, although sodium-rich feldspars may be in an intermediate form, those close to pure albite in composition are generally in the low-temperature form. One problem which arises if this hypothesis is accepted is that of the fairly common occurrence of intermediate-temperature potassium feldspars in contrast with the rarity of intermediate-temperature albites. The most probable explanation for this is that Al-Si ordering is accomplished at higher temperatures in the case of sodium feldspar and so is more readily carried to its limit. Tuttle and Bowen (1950) found that low-temperature albite could be transformed to a higher temperature form above 700°C; whereas Goldsmith and Laves (1954a) effected the change from a microcline to a higher temperature form at 525°C. These values indicate that a comparable degree of ordering in sodium feldspar is accomplished at higher temperature, although the exact significance of these values cannot be explained at the present time.

The hypothesis of a gradual transition from a high-temperature form to a low-temperature form of albite conflicts with the idea of the stable coexistence of two sodium feldspar phases, as for example in some of the microperthites from the Beinn an Dubhaich granite in Skye (Tuttle and Keith, 1954; MacKenzie and Smith, 1956). It is believed that, if perfect equilibrium was maintained in the cooling history of a rock containing feldspars of this type, only one sodium-rich phase of an intermediate form should be present if the rock was quenched from a temperature at which such an intermediate form was stable. After the sodium and potassium phases have segregated in a perthite it is unlikely that perfect equilibrium will be maintained through the cooling of the rock, i.e. that the potassium feldspar released from the sodium-rich phase will be of exactly the same composition as the potassium-rich phase at any instant. In other words, what should be a continuous process under conditions of equilibrium may in fact be accomplished in steps such that the first sodium-rich phase segregated, with some potassium in solid solution, may not be able to achieve the same degree of order as a later exsolved part with a lower potassium content. Although the occurrence of two sodium-rich phases in a perthite is believed to be a non-equilibrium association, it may nevertheless indicate that the feldspar is intermediate between a high-albite perthite and a low-albite perthite, as suggested by Tuttle and Keith (1954).

The variable optical properties of adularias, some microclines and the pericline variety of albite suggest that, certainly at lower crystallization temperatures, feldspars may not always attain the equilibrium form for the rocks in which they occur, and at first sight this might seem to detract from their usefulness as temperature indicators. It is, however, necessary for a good geologic thermometer that the variable which is to be measured should not be too susceptible to temperature changes; otherwise it would generally indicate earth surface temperatures, except in the case of rocks which have been

quenched in a very short time, comparable with that which can be achieved in the laboratory. It is the writer's belief that further studies aimed at understanding the sequence of changes which the feldspars undergo in rock-forming processes will eventually provide petrologists with one of the most valuable geologic thermometers.

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SEDIMENTARY ROCKS OF THE NEWARK GROUP IN THE CHERRY BROOK VALLEY, CANTON CENTER, CONNECTICUT*

JAMES N. PLATT, Jr.

ABSTRACT. Sedimentary rocks belonging to the Newark group of Triassic age have been discovered in a small basin in the town of Canton, Connecticut. These rocks are approximately 1-1/4 miles west of the outcrops of the Newark group in the Connecticut valley. They are composed of red sandstone, arkose, shale, and conglomerate, but without the igneous rocks generally associated with sedimentary rocks of the Newark group. The beds of the basin dip 12 to 17 degrees southeastward, and are abruptly terminated at the eastern edge of the basin where there is a topographic lineament that probably represents a high-angle fault. This fault probably forms the eastern edge of the Cherry Brook basin in the same manner in which the "Great Fault" forms the eastern edge of the Connecticut valley basin.

INTRODUCTION

Rocks of Triassic age occupy numerous basins along the Atlantic coast of North America from South Carolina to Nova Scotia. One of the largest of these is that part of the Connecticut valley that extends from the harbor at New Haven almost to the boundary between Massachusetts and Vermont. The only other previously known rocks of Triassic age in Connecticut are in the Pomperaug valley, a minor sedimentary basin. This basin lies 12 miles west of the Connecticut valley basin in the southwestern part of the state. A second minor sedimentary basin of Triassic age has recently been found by the author in the middle part of the Cherry Brook valley, in the town of Canton, Connecticut. This basin is here referred to as the Cherry Brook basin.

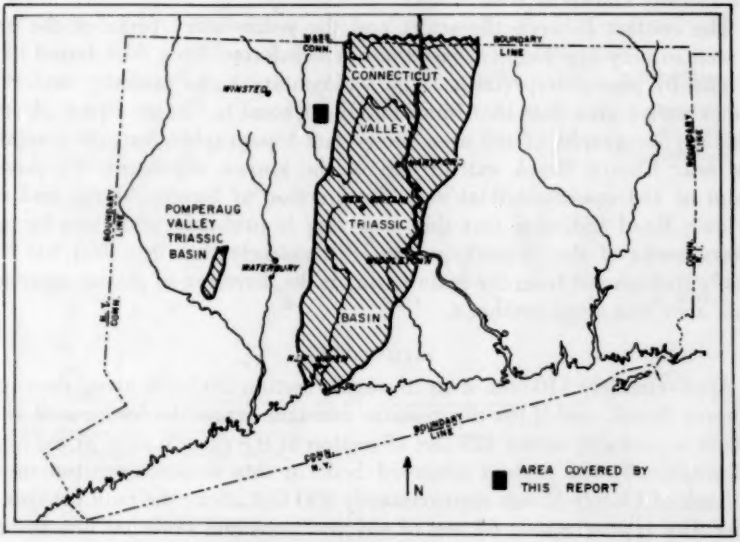

Fig. 1. Index map of Triassic basins in Connecticut.

* Publication authorized by the Director, U. S. Geological Survey.

Approximately four days, during the first two weeks of August 1956, were spent in examining the rocks of the mapped area. The outcrops of the rocks of Triassic age were made more discernible than previously by the removal of much surficial material during the floods of 1955.

THE CHERRY BROOK BASIN

The Cherry Brook basin is very small in comparison to the other two basins of sedimentary rocks of Triassic age in Connecticut. The area that it is believed to cover is approximately 0.3 of a square mile. This may be compared to the estimated 14 square miles of the Pomperaug basin and the 1,311 square miles of the Connecticut valley basin (Krynine, p. 9). It is possible that the rocks of Triassic age in the Cherry Brook basin cover a larger area than that shown on figure 2, but only this small area could be found during the very limited field examination.

The Cherry Brook basin lies on the borders of the U. S. Geological Survey Collinsville and New Hartford 7½-minute quadrangle sheets, and its eastern edge lies approximately 1¼ miles west of the contact between the Newark group of the Connecticut valley and the Hoosac schist of the Western Crystalline Highlands, mapped as Hartland schist by Rodgers et al (1956). The sedimentary rocks have been preserved in a depression in the crystalline rocks, which underlie the basin and form prominent ridges on three sides of it. The rocks of the Newark group weather rapidly and are expressed by low rounded hills, generally covered by glacial deposits, and very few outcrops. The only outcrops known to the author are in and along Cherry Brook for a distance of approximately half a mile north of the twin bridges on Sweeton Road (locally known as West Road).

The contact between the schist and the sedimentary rocks of the basin was seen in only one locality; elsewhere it is inferred from float found in the field and by photointerpretation. The sedimentary rocks probably underlie a more extensive area than that immediately adjacent to Cherry Brook. A study of aerial photographs of the area shows that topographic features similar to those near Cherry Brook extend east of the known exposures. An unusual amount of red sandstone float near the junction of Sweeton Road and Barbourtown Road indicates that this area also is probably underlain by sedimentary rocks of the Newark group. It is unlikely that this float has been glacially transported from the main basin, as the direction of glacial movement in this area was south-southeast.

LITHOLOGY

Approximately 110 feet of stratigraphic section is visible along the course of Cherry Brook, and if the dip remains constant across the basin, as it seems to, there is probably about 425 feet of section at the eastern edge of the basin. Stratigraphically the highest observed beds in this section crop out on the west bank of Cherry Brook approximately 400 feet above the twin bridges. At this locality approximately 64 feet of red sandstone and shale are interbedded. Beds of sandstone as much as 30 inches thick compose the greater part of the section. Shale interbedded with the sandstone forms layers generally not over

3 inches thick. Near the bottom of this exposure the red sandstone grades into purple to gray arkose in beds as much as 6 feet thick.

The arkose, sandstone, and shale crop out for 200 feet in the stream bed and on the east bank of the brook approximately 800 feet north of the bridges. At this locality approximately 27 feet of section is visible, mostly arkose with a few beds of red sandstone near the base of the exposure. The stream flows

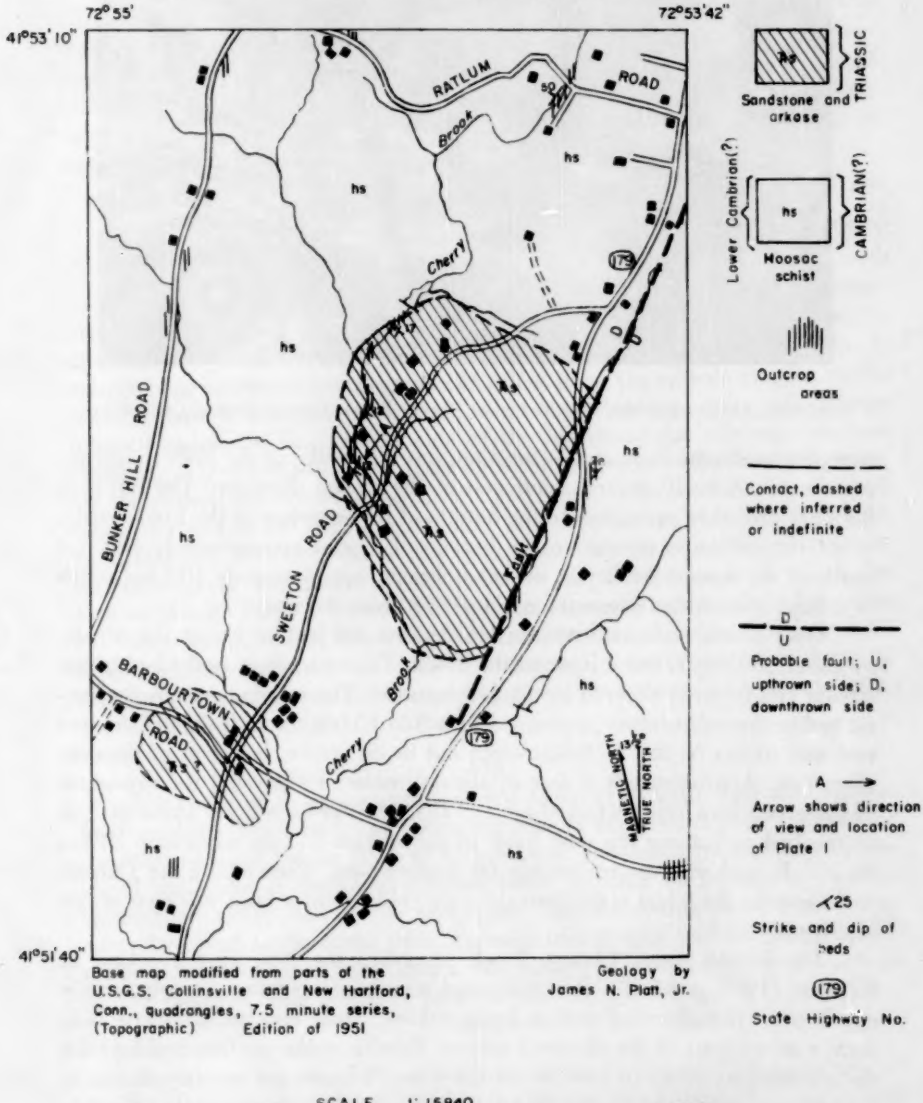

Fig. 2. Geologic map of part of the Cherry Brook valley, Connecticut.

PLATE 1

Sandstone, arkose, and shale in the bed of Cherry Brook, Canton Center, Connecticut.

over the sandstone beds at this location, and the strike of the beds trends approximately 8 to 10 degrees southwest of the stream direction. The top beds here are probably equivalent to the bottom of the sequence in the first locality.

Gray arkose is present in the bottom of a pool approximately 400 feet north of the second locality in the main stream, approximately 100 feet north of a small stream that enters the main stream from the west.

Gray arkose and conglomerate are exposed 300 feet farther up the stream, or about 200 feet below a dam on the brook. This outcrop is in the bed of the stream and is partly covered by alluvial material. The conglomerate is the lowest bed in the sedimentary sequence and is 8 to 10 feet thick. It dips 17 degrees east and strikes N. 32° E. Schist crops out in the stream bed west of the conglomerate. Approximately 6 feet of alluvial material separated the exposures of these two rock types when observed. The schist crops out for about 50 feet in the bed and along the west bank of the stream and its schistosity strikes N. 35° E. and dips approximately 60 degrees west. Presumably the Triassic rocks overlie the schist unconformably; no evidence of a fault was seen at this locality.

The section along Cherry Brook resembles the New Haven arkose of Krynine (1950, p. 37-57). It is composed mainly of sandstone, approximately one-third of the observed section being arkose. Shale and conglomerate beds form a minor part of the observed section. Basaltic rocks are interbedded with the sedimentary rocks in both of the other two Triassic sedimentary basins in Connecticut, but in the Cherry Brook basin the basalt is absent, and no basaltic float has been found downstream from the basin.

THIN-SECTION ANALYSIS

Examination of a thin section of the red sandstone shows that the rock is composed predominantly of quartz. A few grains of plagioclase feldspar and microcline are present, but all are altered to some extent. A few particles of schist also are present. All the grains are angular to subangular and are cemented with a ferruginous clay.

The examination of several thin sections of arkose shows that the rock is composed mainly of plagioclase feldspar altered in varying degrees. Approximately 20 to 30 percent of the rock is composed of quartz; a few grains of microcline, albite, biotite, and garnet plus smaller amounts of other accessory minerals also occur. The grains are moderately well sorted, are angular to subangular, and have very little pore space between them.

STRUCTURE

The structure of the sedimentary rocks of the Cherry Brook basin is similar to that of the other rocks of Triassic age in Connecticut as described by Krynine (1950, p. 117-123). The sandstone, shale, arkose, and conglomerate beds all dip 12 to 17 degrees to the southeast. The small differences in attitude of beds may be the result either of slight folding or of initial dip. A topographic lineament several miles long lies along the eastern margin of the basin. It probably represents a fault, as the topography is quite different on opposite sides. On the western side of the lineament the hills are low and rounded, very characteristic of areas underlain by rocks of the Newark group. On the eastern side the hills rise steeply and schist crops out in the stream bed a few feet east of the fault line and also in a road cut on State Highway 179, approximately 300 feet east of the fault line. This fault probably forms the eastern edge of the Cherry Brook basin in the same manner in which the Eastern Border Fault ("Great Fault") forms the eastern edge of the Connecticut valley basin, and as the several faults described by Hobbs (1901, p. 103-104) form the eastern edge of the Pomperaug basin. From the evidence at hand it is concluded that this lineament probably represents a high-angle fault, the eastern side of which is upthrown.

AGE

The rocks of this basin are believed to be of Triassic age, although no fossil evidence has been found. They resemble in many ways other rocks along the Atlantic Coast known to be of Triassic age. The similarity and the proximity of the rocks of the Cherry Brook basin to rocks of Triassic age of the Connecticut valley lead to the assumption that the sediments in both basins were deposited at the same time. Fossil evidence may well be found in the rocks of this basin, as dark shales are present. Fossils have been found in similar shales in other basins of Triassic age.

SUMMARY

Sandstone, arkose, shale, and conglomerate of Triassic age belonging to the Newark group have been found in the Cherry Brook basin. This basin may include a small area of probable Triassic rocks near the junction of Sweeton

and Barbourtown roads; however, this fact has not been definitely established, and more field work will be necessary before the question can be answered. The contact between a conglomerate of the Newark group and the Hoosac schist has been located in the bed of Cherry Brook; however, a thin mantle of alluvial material covers the actual contact. No basaltic rocks have been observed in this basin, which may mean that the sediments were deposited before the intrusions of Triassic igneous rocks. The sandtone and arkose are probably composed of the weathering products of the adjacent schist, as the mineral compositions are similar and the grains of the sedimentary rocks are angular to subangular, leading to the inference that they have not been transported very far. A high-angle fault probably forms the eastern boundary of the basin with the schist upthrown and the sedimentary rocks downthrown in very much the same manner as the Great Fault bounds the Connecticut valley.

The Cherry Brook basin demonstrates the possibility that still more undiscovered rocks of Triassic age may exist in the Western Crystalline Highlands. In itself, it adds a little information for reconstructing the geologic history of Connecticut.

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REVIEWS

The Pursuit of Science in Revolutionary America, 1735-1789; by BROOKE HINDLE. P. xi, 410. Chapel Hill, N. C., 1956 (University of North Carolina Press, $7.50).—The development of the history of science as an accepted and respectable field of intellectual endeavour is almost entirely confined to the twentieth century. During the past fifty years, a handful of scholars has diligently attempted to lay bare the main lines of scientific development throughout the ages. But with over thirty centuries of almost untapped riches from which to choose, there has been, understandably, a concentration on those epochs or persons whose scientific contributions have been revolutionary.

There is still an enormous amount of work to be done in the delineation of these fundamental aspects of the history of science, but the experience of the twentieth century has served to broaden perspectives and indicate the importance of the tributary branches of the history of science in the understanding of the main stream itself. Specifically, there has been a growing awareness that science, like art, literature or politics both affects and is affected by the total human environment at any period in time. This being so, it is no longer possible to see the history of science simply as a chronicle of successive discoveries; there must be, rather, a greater sensitivity to the complexities involved in the growth of science and a realization that failures can often be as important as successes in understanding the life of science. *The Pursuit of Science in Revolutionary America* is a study of one of these failures. Basically, Professor Hindle sets out to discover what facilities for the pursuit of science existed in Revolutionary America and why science never really flourished in the New World in the eighteenth century. This volume, therefore, has two aspects; it is a history of scientific institutions as well as an attempt to account for the peculiar characteristics of American science (or lack of it). It is well to point out what this book is not: it is not an account of scientific ideas themselves or of the internal development of the sciences in the eighteenth century. Thus, while there is a whole chapter devoted to, and continual reference made to the transits of Venus and Mercury, the reader will find no detailed account of what the transit was, why it was important, or how it was to be used to add to man's store of scientific knowledge.

Professor Hindle's tracing of the history of the development of institutions devoted, in whole or in part, to the furtherance of the sciences in America is exemplary. Exhaustively documented and developed in detail, this major portion of the book gives the only full account of the institutionalizing of science in America.

The attempt to account for the poor showing of American science is somewhat less successful. To be sure, the isolation and relative poverty of the American colonies no doubt served to hinder scientific development. But the main deterrent, according to Professor Hindle, was the emphasis on utility which already in the eighteenth century supposedly marked the American character. According to this view, only those sciences were cultivated which offered the lure of immediate and profitable application. It is this which accounts for the languishing of the sciences in revolutionary America for, in the eighteenth century, there was very little possibility of applying science to practical concerns. Yet, is it not strange that by far the greater part of the

history of American science is marked by its utter uselessness? What could be more useless, at the time, than Franklin's fiddling with Leyden jars, or Wilson's and Audobon's ornithology, or Marsh's and Cope's "bone hunting"? The principle of utility seems to fall short here.

A short bibliographical essay and an index complete a book valuable to all interested in the American past and our cultural development.

L. PEARCE WILLIAMS

Arizona's Meteorite Crater—Past, present, and future; by H. H. NININGER. P. xvi, 232; 48 pls. Sedona, Ariz. (American Meteorite Museum, $3.75). —This book recounts in a pleasant, narrative style its author's experiences and opinions resulting from a lifelong association with meteorite collecting, especially about the Arizona crater. The history of the crater is told, from its discovery in the 1870's to the present.

The new information in this book is certainly important enough to justify publication. Nininger and his associates have apparently found a substantial new portion of the "corpus delicti" of the main meteorite mass, in the form of highly nickeliferous, metallic spheroids that must have condensed from vapor soon after the impact. These spheroids are from 0.1 to 2.0 mm in diameter; their preservation substantially unoxidized seems to the reviewer likely to be due partly to their high tenor of nickel (17%) and cobalt (2.2%). Nininger estimates that there must be 4000 to 8000 tons of spheroids in the upper 4 inches of soil within 2.5 miles of the crater rim. He estimates further that this is the residue from an original deposit in excess of 100,000 tons, a very considerable quantity. A still further contribution is the excellent record of Nininger's careful search for, and finding of, extensive deposits of glossy, slag-like *impactite* particles in the explosion-rubble about the crater; he describes their shapes and other characteristics.

One feels a considerable measure of sympathy for Nininger's proposition that the crater should be made into a National Monument for its own preservation and for the best enjoyment and education of the public.

HORACE WINCHELL

Les Dislocations; by J. FRIEDEL. P. viii, 314; 145 figs., Paris, 1956 (Gauthier-Villars, 3500 fr. ($10.20) paper; 3800 fr. ($11.05) bound).—The preparation of a full-scale textbook on dislocations seems especially fitting at present because, as the author says, the subject has evolved enough in the last few years to warrant more than a mere translation of some foreign works. It will be surprising indeed if this work fails to inspire important contributions, both practical and theoretical. Although the author modestly proclaims his depedence upon a number of well known English, Belgian, American, and other contributors, his own service in assembling all the data and in treating each section critically and comparatively, will be appreciated by French-speaking readers in particular, but in general by many others who have needed a textbook-treatment for reference purposes. Friedel is not only thorough in his descriptive treatment, but also careful in his documentation. A list (p. vii) of

ten books, and nine general articles on dislocations includes a surprisingly large number in English (all but four items published in England or the United States).

The following chapter headings, somewhat condensed and abbreviated, show the scope of the treatment: Part I, (p. 1-134), general properties of dislocations, contains chapters on definitions, elastic theory, movement, imperfect dislocations, and crystal growth; Part II (p. 135-148), groups of dislocations, covers polygonization and mosaic structure, cold working and piling up of dislocations, tempering and drawing related to recrystallization, plastic flow, and cleavage. Part III (p. 227-284), interactions of dislocations and impurities, includes introductory definitions, hardness under stated conditions, formation and movement of clouds of impurities, and influence of dislocations on other types of lattice imperfections. Appendices follow on elasticity; on certain physical properties of common chemical elements solid at room temperature; on gliding and twinning elements in simple crystal structures; and a short glossary of French, English, and German equivalents. A 10-page bibliography, a 2½-page alphabetical index, and a 6-page table of contents complete the volume.

One feels a considerable satisfaction in studying this book because it is a scholarly, thorough, and practical work on a most important subject.

HORACE WINCHELL

Pennsylvanian Geology of the Cumberland Plateau; by CHARLES W. WILSON, JR., JOHN W. JEWELL, and EDWARD T. LUTHER. P. 21 (26 x 21 in), 15 pls. Nashville, Tennessee, 1956 (Tennessee Division of Geology, $2.00).—This report, presented in folio form, contains a detailed revision of the Pennsylvanian stratigraphy of Tennessee, illustrated with isopach maps of the principal subdivisions and distribution maps of the main sandstone and conglomerate units; a new geologic map of the Pennsylvanian area on the Cumberland Plateau in Tennessee (scale 1 inch to 3 miles, on 4 sheets), using the new subdivisions; and small-scale structural maps that illustrate the by no means negligible structural features of the Plateau. It is based on detailed geologic mapping of several key areas, tied together with more general reconnaissance, all relatively recent; two of the detailed studies are published in Tennessee Division of Geology Bulletin 60 (1954), which includes much structural detail, and Folio 1 (1956), which institutes a series of Geologic Quadrangle Maps of the state. With this publication, the Tennessee Division of Geology, one of the most active of the state geological surveys, presents in summary the latest information on another large segment of its richly varied state.

JOHN RODGERS

Publications Recently Received

Cours de Géometrie Différentielle Locale; by J. Favard. Paris, 1957 (Gauthier-Villars, 6.000 fr.).

The Barker Index of Crystals, Volume II, Monoclinic System; by M. W. Porter and R. C. Spiller. Part 1, Introduction and Tables; Part 2, Crystal Descriptions M. 1 to M. 1800; Part 3, Crystal Descriptions M. 1801 to M. 3572. Cambridge, 1957 (W. Heffer & Sons, £10 the three parts).

Stress and Strain in Bones; by F. Gaynor Evans. Springfield, Illinois, 1957 (Charles C. Thomas, $6.50).

Basic Foundations of Isotope Technique for Technicians; by Willard C. Smullen. Springfield, Illinois, 1957 (Charles C. Thomas, $4.75).

Mio-Pliocene Floras From West-Central Nevada; by Daniel I. Axelrod. Berlekey, 1957 University of California Press, $7.50).

Einführung in die Allgemeine Biologie; by Max Hartmann. Berlin, 1957 (Walter de Gruyter & Co., DM 2,40).

Engineering Enrollment in the United States; by Norman N. Barish. New York, 1957 (New York University Press, $7.50).

General Geography for Colleges; by O. D. Von Engeln and Bruce C. Netschert. New York, 1957 (Harper & Bros., $7.50).

Irradiation Colours and Luminescence; by K. Przibram. London, New York, 1957 (Pergamon Press, $10.00).

Arizona's Meteorite Crater; by H. H. Nininger. Sedona, Arizona, 1957 (American Meteorite Museum, $3.75).

Farmdale Drift in Northwestern Illinois; by Paul R. Shaffer. Illinois Geol. Survey Rept. of Inv. 198. Urbana, 1956.

A History of the Ancient Southwest; by Harold Sterling Gladwin. Freeport, Mr., 1957 (Bond Wheelwright Co., $8.50).

Genetic Studies with Bacteria; by M. Demerec, Zlata Hartman, Philip E. Hartman, Takashi Yura, Joseph S. Gots, Haruo Ozeki and S. W. Glover. Washington, D. C., 1956 (Carnegie Inst. of Washington Pub. 612, $ .80 paper bound, $1.00 cloth bound).

U. S. Geological Survey Bulletins: 1000-E, Geochemical Studies in the Southwestern Wisconsin Zinc-Lead Area; by V. C. Kennedy ($1.00). 1016, The Wishbone Hill District, Matanuska Coal Field, Alaska; by F. F. Barnes and T. G. Payne ($2.50). 1021-H, Annotated Bibliography of Alaskan Paleozoic Paleontology; by J. T. Dutro, Jr. ($ .40). 1021-I, Geology of Devils Tower National Monument, Wyoming; by C. S. Robinson ($ .50). 1021-J, The Problem of the Cochrane in Late Pleistocene Chronology; by T. N. V. Karlstrom ($ .30). 1023, Bentonite Deposits in Marine Cretaceous Formations, Hardin District, Montana and Wyoming; by M. M. Knechtel and S. H. Patterson ($1.50). 1024-D, Magnetite Deposits at Tuxedni Bay, Alaska; by Arthur Grantz ($ .15). 1024-E, Pyrite Deposits at Horshoe Bay, Latouche Island, Alaska; by F. A. Stejer ($ .45). 1027-B, Geology of the Crazy Woman Creek Area, Johnson County, Wyoming; by R. K. Hose ($1.75). 1027-J, Geology of the Stanford-Hobson Area, Central Montana; by J. D. Vine ($1.25). 1027-L, Oil and Gas Wells Drilled in Southwestern Virginia before 1950; by J. W. Huddle, E. T. Jacobsen, and A. D. Williamson ($ .25). 1027-M, Reconnaissance Geology of Western Mineral County, Montana; by R. E. Wallace and J. W. Hosterman ($1.25). 1027-N, Mineral Resources of the San Carlos Indian Reservation, Arizona; by C. S. Bromfield and A. F. Shride ($1.25). 1027-O, Thorium and Rare-Earth Minerals in Powderhorn District, Gunnison County, Colorado ($ .60). 1027-P, Geology of the Murray Area, Shoshone County, Idaho; by J. W. Hosterman ($1.00). 1028-C, Geology of Northern Adak Island, Alaska; by R. R. Coates ($1.50). 1028-D, Geology of Northern Kanaga Island, Alaska; by R. R. Coates ($ .75). 1028-E, Reconnaissance Geology of Some Western Aleutian Islands, Alaska; by R. R. Coates ($ .75). 1030-D, Accuracy of Ore-Reserve Estimates for Uranium-Vanadium Deposits on the Colorado Plateau; by A. L. Bush and H. K. Stager ($ .45). 1030-F, Geology and Monazite Content of the Goodrich Quartzite, Palmer Area, Marquette County, Michigan; by R. C. Vickers ($ .50). 1030-G, Wall-Rock Control of Certain Pitchblende Deposits in Golden Gate Canyon, Jefferson County, Colorado; by J. W. Adams and Frederick Stugard, Jr. ($ .50). 1032-B, Geology and Ore Deposits of the Freeland-Lamartine District, Clear Creek County, Colorado; by J. E. Harrison and J. D. Wells ($1.50). 1036-F, A Spectrographic Method for Determining the Hafnium-Zirconium Ratio in Zircon; by C. L. Waring and H. W. Worthing ($ .15). 1036-H, The Occurrence of Minor Elements in Ash of Low-Rank Coal from Texas, Colorado, North Dakota and South Dakota; by Maurice Deul and C. S. Annell ($ .25). 1038, Geology and Mineral Resources of the Hudson and Maynard Quadrangles, Massachusetts; by W. R. Hansen ($1.75). 1039-A, Marl Deposits in the Knik Arm Area, Alaska; by R. M. Moxham and R. A. Eckhart ($ .50). 1039-B, Occurrence of Diatomaceous Earth near Kenai, Alaska; by George Plafker ($ .75). 1042-A, Geology of the Johnson Creek Quadrangle, Caribou County, Idaho; by R. A. Gulbrandsen, K. P. McLaughlin, F. S. Honkala, and S. E. Clabaugh ($ .75). 1042-B, Airborne and Ground Reconnaissance of Part of the Syenite Complex near Wausau, Wisconsin by R. C. Vickers ($ .15). Washington, 1955 and 1956.

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